ECONOMIC GEOLOGY

WITH WHICH IS INCORPORATED

THE AMERICAN GEOLOGIST

VOL. IX SEPTEMBER, 1914 No. 6

PETROGRAPHICAL NOTES ON THE SUDBURY NICKEL DEPOSITS.

ERNEST HOWE.

INTRODUCTION.

In the autumn of 1911 J. D. Irving and the writer visited a number of the well-known deposits of copper- and nickel-bearing sulphides near Sudbury, Ontario. Through the courtesy of the officials of the Canadian Copper Company and the Mond Nickel Company they were given every facility for studying the geology of the ore-deposits and were enabled to collect a series of characteristic specimens. Pressure of other work has prevented a study of the collections until the past year, when the writer revisited some of the localities and collected more material.

There are many problems in the petrology and economic geology of this region that are not only of absorbing interest but are so closely related to one another that it is all but impossible to take up the study of any one without considering, to some extent, the others as well. In the present paper attention is confined as much as possible to certain petrological features of the sulphide masses and associated rocks, and to the bearing that these relations seem to have on the origin of the ore-deposits. A revision of the work of Coleman, Barlow, and their associates has in no way been considered.

GEOLOGY OF THE DISTRICT.

The principal geological features of the Sudbury region have been so thoroughly described by Coleman, Barlow, Walker, Dickson, and others that only a brief summary is necessary.[1]

As interpreted by the Canadian geologists, the rock with which the ores are so intimately associated is a norite intruded in the form of a laccolith between Upper Huronian sediments and ancient crystallines. A marked subsidence of the central portion of the laccolith followed soon after the injection of the magma, and subsequent erosion has exposed the border of the norite mass as a band one to four miles wide which surrounds the Huronian sediments. In other words, the intrusive may be regarded as roughly spoon-shaped with its rim only exposed; the greater diameter, northeast-southwest, is about thirty-eight miles and the shorter diameter fifteen miles. The outer surface of this spoon is in contact with a complex of ancient greenstones and associated granites and gabbros, and along the contact or close to it the ore-deposits are found. Between the Upper Huronian rocks and the norite proper within the ellipse the rocks are of the composition of granites; they are characterized by micrographic intergrowths of quartz and feldspar and are considered to be a part of the laccolithic mass, representing a differentiation *in situ*. The rock of this portion of the laccolith is often spoken of as "micropegmatite" in order to distinguish it from the norite that forms the lower or outer part of the body. The masses of pyrrhotite, chalcopyrite and pentlandite that constitute the ore-deposits are regarded as segregations from the norite magma following its intrusion.

[1] Coleman, A. P., *An. Rep. Ont. Bur. Mines*, 1903, pp. 235–290; *Rep. Ont. Bur. Mines*, Vol. 14, Pt. 3, 1905; "The Sudbury Laccolithic Sheet," *Jour. Geol.*, Vol. 15, pp. 759–782, 1907; "The Nickel Industry," Can. Dept. Mines, Mines Branch, No. 170, 1913. Barlow, A. E., "On the Origin and Relations of the Nickel and Copper Deposits of Sudbury, Ontario," ECON. GEOL., Vol. I., pp. 454–466, 545–553, 1906; Geol. Survey of Canada, No. 961, 1907 (reprint). Walker, T. L., "Geological and Petrographical Studies of the Sudbury Nickel District," *Q. Jour. Geol. Soc.*, Vol. 53 (1897), pp. 40–66. Dickson, C. W., "The Ore-Deposits of Sudbury, Ontario," Trans. A. I. M. E., Vol. 34, pp. 3–67 (1903); "Genetic Relations of Nickel-Copper Ores," *Jour. Can. Min. Inst.*, Vol. 9, pp. 236–260 (1906).

The Creighton ore-body is typical of those occurring near the periphery of the main norite mass. It has been worked as an open pit 650 feet in length and from 100 to 400 feet in width to a depth of some 300 feet, below which are underground workings that have developed ore farther to the southwest. The ore, which lies between a coarse-grained gneissoid granite on the foot and norite on the ill-defined hanging wall, consists of a nearly solid mass of pyrrhotite and chalcopyrite; pyrrhotite predominates, and with it is associated the nickel mineral, pentlandite, which, however, can seldom be recognized megascopically.

The Frood and Stobie ore-bodies are associated with a more or less continuous, narrow band of norite that is nearly parallel to the lower or outer contact of the main norite mass, and separated from it by about a mile of granite and greenstone. The presence in depth of large bodies of (highly) nickeliferous ore has been proved by diamond drills. At the surface the norite shows disseminated pyrrhotite, at many places the sulphide being abundant enough to have developed a well-marked gossan.

Another type of offset deposit is that of the old Copper Cliff and also the Victoria. At the latter, according to Coleman,[1] 'columns,' or pipe-like bodies of ore, have been traced almost vertically downward for more than 1400 feet. Although not far distant from the norite, the country rock appears to consist of various kinds of greenstone.

The origin of these deposits has, from the time of their discovery, been the subject of much discussion. Most of the Canadian geologists, who have devoted a great deal of time to the problem, hold that the enormous masses of pyrrhotite and chalcopyrite are of igneous origin, having segregated, largely through the influence of gravity, while in a molten condition from the norite magma with which the field relations indicate they are so intimately associated. Others regard the deposits as wholly epigenetic and the result of metasomatic processes. The advocates of the theory of magmatic origin of the ores base their opinions largely on the evidence of field relationships, and insist that

[1] Coleman, A. P., "The Nickel Industry," pp. 36–37, 42–44, Canada, Dept. of Mines, Mines Branch, No. 170, 1913.

those who favor the theory of aqueous or metasomatic origin have confined their attentions principally to microscopical studies of the ores and rocks.

For reasons that are given later, the writer was not convinced by the field evidence at Creighton of the blending of sulphides and norite at the hanging wall, but was impressed by the apparent original character of the sulphides in the Frood rock that has been shown by drilling to grade downward into a large body of ore.

FROOD.

The general appearance of the sulphide impregnated Frood rock that is too low grade to be considered ore is that of a medium grained diorite with a suggestion of gneissoid texture, throughout which patches of sulphides 5 millimeters in diameter are disseminated with great regularity. On fresh surfaces the untarnished grains of pyrrhotite stand out in marked contrast to the dark gray of the silicates and give the rock a porphyritic appearance.

The Frood rock is puzzling because it shows microscopically both original and secondary minerals, and evidences of both dynamic metamorphism and replacement. It illustrates many of the features that have been regarded as proving the epigenetic character of the Sudbury ores and, although the evidence is not conclusive, it offers serious objections to the confirmation of the view held in the field that the sulphides in the Frood rock were of magmatic origin.

Thin sections show that the rock consists of nearly equal amounts of plagioclase (Ab_5An_3—Ab_2An_3), quartz, hornblende, and biotite, with an abundance of magnetite and apatite. Pyrrhotite and chalcopyrite together may make up ten per cent. of the rock.

Some of the hornblende is strongly pleochroic, blue-green to yellow-green, and massive with well-marked prismatic cleavage; much of it is nearly colorless in granular masses and fibrous aggregates. This hornblende possesses many of the characteristics of amphibole derived from pyroxene so common in basic

rocks that have undergone deep-seated metamorphism, but in the process every trace of the original mineral has disappeared. The norites elsewhere often show the pyroxenes changing to hornblende, and it is not unlikely that the hornblende of the Frood rock may have had a like origin.

Biotite occurs in irregular-shaped patches or in blades with the basal planes well developed. It is frequently included in hornblende or associated with the hornblende aggregates. Inclusions of magnetite are abundant and pleochroic halos are very common. A part of the biotite is probably secondary; whether or not any of it is original is impossible to say. Biotite, apparently magmatic, is found in the fresh norite where it encloses pyroxene and magnetite and also has pleochroic halos.

Plagioclase crystals are stubby and from 0.1 to 2 millimeters in length; nearly all are zonal. There is considerable variation in their composition, which may range from labradorite-bytownite at the interior of some of the strongly zoned crystals, to oligoclase-albite in net-like, micrographic intergrowths with quartz. The outer shells of many of the zoned feldspars are very commonly unstriated; the interiors show evidence of slight absorption while the exteriors more often have good crystallographic boundaries, although they too have in some instances been corroded. Usually grouped together, or associated with quartz, the feldspars are also found in the centers of hornblende aggregates and included in biotite. It is doubtful if any orthoclase is present.

Quartz is abundant, and there are numerous subhedral crystals and grains of magnetite or ilmenite present as inclusions in the other minerals. Apatite is a conspicuous accessory.

It has been said that the Frood rock shows in places a more or less well defined gneissoid structure. Thin sections confirm this in a general way; in some the patches of hornblende are elongate and roughly parallel, in others this feature is less noticeable, and seems to be lacking with the other minerals. The clearest indication that the rock has suffered dynamic metamorphism is found in the fine, nearly parallel cracks or fractures best seen in the quartz and feldspar groups, but also to be traced in the more massive hornblende and not infrequently in the larger apatite

crystals. Microscopically there appears to have been no elongation by recrystallization of the minerals parallel to this fracture system. The squeezing resulted merely in the development of incipient fracture and strain with practically no crushing and no recrystallization. If the hornblende and certain of the other minerals formed as a result of dynamic metamorphism it must have been at an earlier period.

A question of importance in connection with the sulphides is the origin of the quartz that is so very abundant in the Frood rock. In many portions of the thin sections quartz occurs in poikilitic masses two to four millimeters in diameter, the outlines of which are irregularly serrated; in some instances rude rhombohedral outlines can be made out. The inclusions are plagioclase feldspars and a very little apatite and biotite. The feldspars are usually in detached crystals considerably corroded, though occasionally a net-like form, apparently oligoclase-albite or andesine, may be made out that suggests micrographic intergrowth. The feldspars are generally strongly zoned and it can be said confidently that they are original constituents of the rock, that two periods of generation are shown, and also that they have suffered corrosion or attrition since the development of the outer zones. Although the quartz often shows pronounced strain-shadows, the feldspars have not been crushed or fractured and are practically without strain; with quartz and hornblende they exhibit the fine, nearly parallel cracks of relatively recent origin, and it is evident that their relation to the quartz had been determined before the late period of compression to which this slight fracturing is attributed. It is believed that quartz of this character is an original constituent of the rock; it occurs in essentially the same way in fresh norite both close to and far from the ore-bodies. In addition to this quartz there is a small but definite amount that is undoubtedly secondary, being associated with the secondary hornblende, while one section showed a minute veinlet younger than any of the other minerals but traversed by the nearly parallel fractures common to the older minerals. Whether this quartz is to be regarded as a metamorphic mineral derived from the other silicates, or has been introduced from

without it is impossible to say, but the general absence of minerals usually associated with metasomatic processes favors the former view.

The weight of evidence seems to indicate that the Frood rock has been more or less crushed and recrystaliized as a result of dynamic metamorphism, and that since recrystallization it has been subjected to further but less intense pressure which developed a system of parallel fractures hardly sufficient to account for the megascopic gneissoid texture, for the origin of which one must look to the earlier stage of metamorphism.

The sulphides, pyrrhotite and chalcopyrite, occur in several ways: as large irregular masses (1–5 mm.), interstitial or moulded on other minerals; in small (0.05–0.1 mm.) grains included in biotite, hornblende and quartz, and often intergrown with magnetite; in minute rounded particles or blebs (0.002–0.005 mm.) arranged in trains or streams which at first might be taken for inclusions in quartz and feldspar but which are in reality unconnected patches in cleavage cracks; and, finally, filling cracks or fractures in hornblende, feldspar and quartz. The last two modes of occurrence are clearly due to solution and redeposition along the fractures formed at the latest stage of dynamic metamorphism. To this period also is to be attributed the only certain instance of replacement noted: that of a nearly perfect crystal of hornblende by chalcopyrite, pyrrhotite and quartz (Fig. 121).

The large masses of sulphides are distributed with great uniformity throughout the rock; they are not connected with one another by veinlets or branches, and they have no regular shapes, but may be in the more gneissoid rock slightly elongate with the greater diameters roughly parallel. The edges of the masses are even and rounded; they are straight or angular only when in contact with crystal faces of biotite, hornblende or feldspar. Pyrrhotite is the dominant mineral and with it chalcopyrite is intergrown. Pentlandite, the nickel-iron sulphide, can seldom be recognized with the ordinary petrographical microscope, although

the metallographic studies of Campbell and Knight[1] show that it is intergrown with the pyrrhotite in most of the specimens that they examined. Inclusions of magnetite, often subhedral, are common, and small crystals of apatite may occasionally be found; less frequently biotite flakes and grains of hornblende or feldspar are present. Nearly all of the larger masses of sulphides are irregularly fractured. As a rule the fractures are closed, but in a few instances the cracks have been filled with a fibrous material that is believed to be hornblende. The elongate sulphide masses in the more gneissoid rock do not seem to be any more fractured than those in the less foliated specimens.

The large masses of sulphides are always more or less completely surrounded by biotite and hornblende, and are less often in contact with quartz and the feldspars. There is nothing in the form of any of the masses to suggest that they have replaced other minerals, nor have they any crystal form of their own.

In addition to the large masses of sulphides, smaller, irregular ones are very common as inclusions in biotite. The biotite varies from 0.5 to 1.5 millimeters in diameters, and the sulphide from 0.075 to 0.25 millimeters. Intergrowths of pyrrhotite and chalcopyrite may form a single inclusion, either may occur alone, and either or both together may be intergrown with magnetite. Similar inclusions may be found in hornblende, but are rare.

The study of the Frood rock has shown that it is dynamically metamorphosed. Although no trace of the unaltered rock has been found it is believed that it must have been related to the norite, since rocks similar to the Frood have been shown to belong to the main norite mass and that their hornblende has been derived from pyroxene.

Because of the metamorphic character of the rock the origin of the sulphides is completely masked. If they were primary constituents of the original rock their relations to the silicates have been so changed by the dynamic metamorphism of the whole rock that no conclusive evidence of their magmatic origin is preserved. In an unmashed rock the intergrowths of magnetite and

[1] Campbell, William, and Knight, C. W., "On the Microstructure of Nickeliferous Pyrrhotites," ECON. GEOL., II., 350–366, 1907.

sulphide included in biotite would be regarded as original, but uncertainty as to the original character of the biotite prevents the acceptance of this evidence. On the other hand it is equally impossible to prove that the sulphides have been introduced into the rock by metasomatic processes. It is true that a small amount of redistribution of the sulphides has taken place, but this was after the system of parallel fractures had been developed. The large masses of pyrrhotite and chalcopyrite have been fractured and the cracks filled with secondary silicates, which suggests that they had nearly their present form at the time the dark silicates were

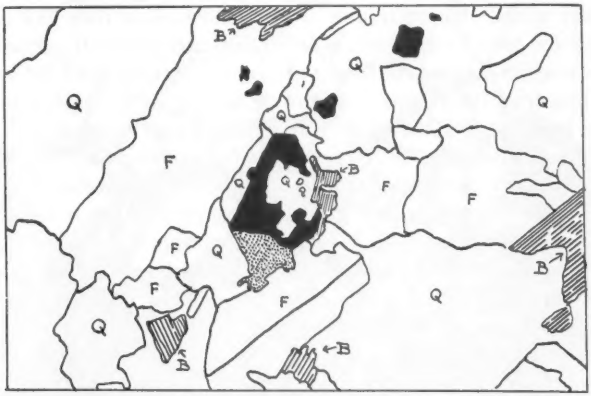


FIG. 121. Camera lucida drawing of coarser grained portion of Frood rock composed of plagioclase feldspar (F), quartz (Q), and biotite (B) with patches of chalcopyrite (black) and pyrrhotite (dotted). In the center chalcopyrite, pyrrhotite and quartz replace a hornblende crystal. × 110.

developed. Although conclusive proof is lacking, it seems not improbable that the sulphides were present in the rock before its partial recrystallization. If they were of metasomatic origin it is likely that the associated minerals and features characteristic of replacement would have been completely changed or obliterated by the deep-seated metamorphism to which the rock as a whole has been subjected. Although the megascopic appearance of the Frood rock suggests that the sulphides and silicates formed con-

temporaneously, the writer believes that the magmatic origin of the sulphides can neither be proved nor disproved by a study of thin-sections.

CREIGHTON.

Aside from the impressive size of the Creighton ore-body, its most striking feature is the character of its contact with the norite of the hanging-wall. At a number of places in the open pit and in stopes at lower levels the change from ore to rock with no sharp line of separation is well shown. The transition may take place within a space of three or four feet, or may extend over as many yards. The character of this gradation of rock into ore calls for special consideration as it constitutes one of the criteria upon which is based the theory of gravity segregation of the sulphides from the magma. According to most of the descriptions one expects to find the nearly pure sulphides pass by imperceptible increase in the quantity of associated silicates into a rock in which sulphides are sparingly present as accessories or altogether absent. While there is undoubtedly a gradual change from ore to rock, it would appear to be due to a mechanical mixture of sulphides and norite in the transition zone and not to a gradation in a mineralogical sense.

In all places where transition from ore to rock is supposed to exist, the norite has been extensively shattered in the neighborhood of the ore, and the sulphides appear to have penetrated the norite along the cracks and fissures so formed, while angular fragments of norite are included in the sulphides close to the rock. The veinlets of sulphides die out gradually in the norite away from the massive ore, while the rock fragments included in the sulphides become less numerous and smaller in size as their distance from the hanging-wall increases (Fig. 122). There is thus a transition from ore to rock in a mechanical sense, and, from a mining standpoint the expression is justifiable. Neither megascopically nor with the aid of the microscope could the writer recognize a petrographical graduation.

The norite near the contact with the ore, and the norite inclusions in the ore are fine grained, suggesting conditions of rela-

tively rapid cooling characteristic of the border zone. Although a point of minor importance, it is difficult to understand how such textures could develop where the cooling norite was separated from the invaded rocks by a mass of molten sulphides.

One of the criteria most commonly used for the recognition of replacement ore-bodies is the presence in the massive ore or vein

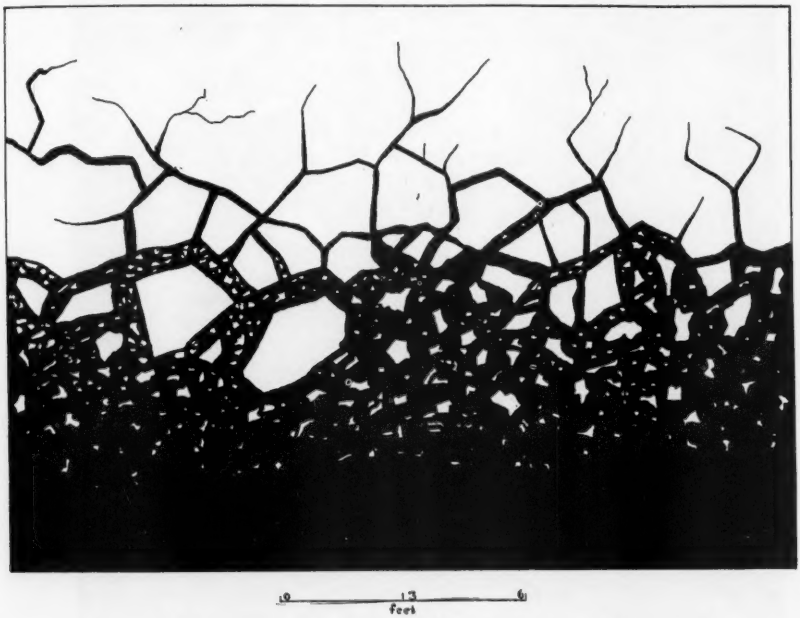


FIG. 122. Diagrammatic drawing illustrating the character of the contact between massive sulphides (black) and norite (white). Creighton, third level, west end of pit. Compare plate XIII.

matter of unsupported fragments of the wall rock. The almost invariable angular character of the fragments of country rock included in the ore near the contact with the norite, from masses several feet in diameter down to particles one quarter of an inch in size does not suggest that they are residual portions of country

PLATE XIII.

HORNBLENDE SCHIST INTRUDED BY GRANITE, NEAR ROCKWOOD, COLORADO. Shows the brecciation of the schist and the angular character of the fragments included in the granite. Twenty feet away the granite is almost free from inclusions. (Howe, U. S. Geological Survey.)

rock that has undergone the extensive replacement necessary to account for ore-bodies of such magnitude. The sharpness of the contact between the sulphides and the norite fragments recalls the familiar conditions found at many intrusive contacts where brecciated fragments of the country rock lie in the intrusive with their angular character almost perfectly preserved. Such a contact breccia is shown in Plate XIII.

Little is known in regard to the physical conditions that might exist at a contact between segregated sulphides and norite magma during the period of solidification of both. We do know that the norite near the contact is fine-grained, and that it appears to have cooled and to have been subsequently shattered before the sulphides solidified. Although it is conceivable that the silicate portion of the intruded magma froze and rested on still molten segregated sulphides, it would seem more reasonable to regard the ore as a later intrusive, if the sulphides are to be recognized as of magmatic origin.

The foot wall of the Creighton ore-body as exposed in the open pit is a medium-grained granite, pinkish to red in color, with a variable amount of biotite and hornblende. Close to the ore it may be more or less impregnated with sulphides, chalcopyrite predominating.

The rock consists of feldspar, quartz, biotite and hornblende in proportions common to most granites. An abundant micrographic intergrowth of quartz and feldspar, however, gives the rock a distinct individuality, while the presence of a sodic plagioclase often in excess of the potash feldspar is also characteristic. The plagioclase is twinned according to the albite and pericline laws and closely resembles ordinary microcline. It is optically positive, however, and this, together with the index of refraction, which is slightly less than balsam, determines it as oligoclase-albite. This is the only feldspar that is present in micrographic intergrowth with quartz.

In all of the thin sections and polished specimens of the massive sulphides that have been studied silicates are present. Mention has already been made of the norite fragments near the hanging wall of the Creighton ore body. As a rule their petro-

graphic character is unmistakably that of fine-grained norite, in most cases fresh. A certain amount of alteration has sometimes taken place about the borders of fragments or along the edges of the massive norite in contact with the sulphides. This appears to consist principally of a change of the pyroxene to hornblende and impregnation by sulphides. A fair proportion of the sections of included fragments is of fine-grained amphibolite.

In addition to these fragments of relatively basic rocks near the hanging wall there are numerous minute patches distinctly different in character scattered throughout the whole mass of the sulphides. They are, perhaps, more abundant near the foot wall granite, but are also present in the center of the ore-body and may constitute from three to ten per cent. by volume of the ore. The first to be observed were in specimens collected to show the relation of the sulphides to the norite inclusions near the hanging wall. A very large majority of these silicates consists of micrographic intergrowths of quartz and oligoclase-albite or albite; in addition there is a lesser quantity of quartz and feldspar in separate particles, and occasional fragments of green hornblende and brown biotite. These patches of silicates vary from 0.1 to 2 millimeters in diameter. The boundaries between the silicates and the sulphides are sharp. In a few cases a slight replacement of the feldspar by sulphide has taken place at the border. The form of the patches of micrographic quartz and feldspar is perhaps best described as subangular; some are distinctly angular, others have curving or rounded outlines. The hornblende and biotite always appear as angular fragments. Rounded octahedra of magnetite, one to one tenth millimeters in diameter, are very abundant; they are shown in Fig. 123 together with the silicates included in the sulphides.

The small patches of micrographic quartz and feldspar that have been described are strikingly shown under the microscope, but are easily overlooked in hand-specimens. There are, however, in many places patches of a coarse grained reddish rock 2 centimeters or more in diameter that are clearly included fragments of the foot wall granite; they were abundant near a large horse of granite on the third level in the northeast corner of the open pit

at Creighton. One specimen from this locality is of special interest; it consists of a fine-grained black rock, 4×8 centimeters, in sharp contact with the sulphides. Near the contact the rock has a border of denser material that seems to be made up largely of hornblende and biotite. The sulphides are filled with small granules of the black rock (1–3 mm.), and in places there is an

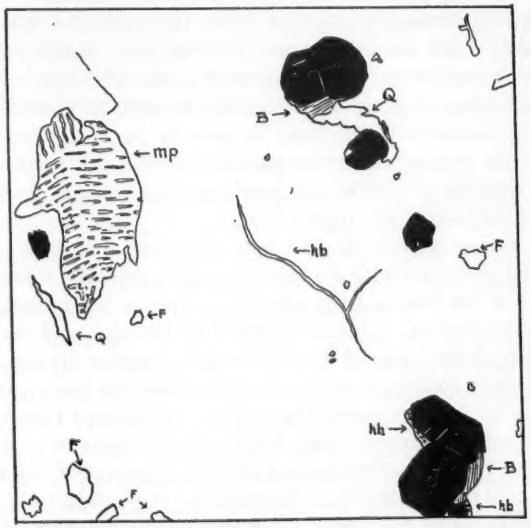


FIG. 123. Thin section of massive pyrrhotite (white) with inclusions of micropegmatite (mp), quartz (Q), feldspar (F), magnetite (black), and biotite (B); secondary hornblende (hb) filling cracks in pyrrhotite, and in cracks and at borders of magnetite. Creighton. $\times 22$.

abundance of the light-colored silicious material also included in the sulphides. Near one corner the black rock is cut by a 15-millimeter vein or dike of medium-grained granitic rock that can not be distinguished from the silicious material associated with the sulphides. At one end this miniature dike is almost free from sulphides but grades, within a few centimeters, into nearly pure sulphide containing a little quartz and feldspar. Another

specimen from the same general locality shows a fragment of the black rock included in the granitic material and the whole enclosed in sulphides.

The microscope shows that the "black rock" fragments are rich in hornblende with a little quartz, biotite, plagioclase and magnetite. They are seldom fresh, and are totally different from norite in which pyroxene has been altered to hornblende.

Assembling these facts one is led to the conclusion that both megascopic and microscopic patches of silicious material represent inclusions of the foot wall granite in the sulphides, and that the inclusions of dense basic rock are in part, at least, of the older greenstones. This must be true in the cases described where the granite either intrudes or includes the basic rock. The gradation of granite into nearly massive sulphide is due to local impregnation and replacement.

The attractive possibility has been considered that the silicious material associated with the sulphides might represent a residual portion of the magma from which the sulphides are supposed to have been derived. This is suggested by the very uniform distribution of this material throughout the Creighton ore-body, by the apparent absence of sharp contacts between the larger patches and the sulphides as contrasted with the well-defined boundaries of the norite fragments, and, finally, by the apparent common intrusion by both sulphides and silicious material of the dark basic rocks that can hardly be distinguished in the field from fine-grained facies of the norite. The microscope, however, shows over and over again the absolute similarity of the acid inclusions to the foot wall granite. Furthermore, the granite is a coarser-grained rock than the norite and greenstones, and the absence of sharp boundaries to the megascopic fragments is easily explained by the irregular fracture of the granite. The microscope shows that the contacts between sulphides and silicates are as sharp as with the more basic rocks, but that the sulphides, more especially chalcopyrite, frequently have entered cracks in the quartz and have replaced the other silicates near the margins. As already stated, the dark basic rocks, best described as greenstones, intruded by or included in the granitic material represent the

country rocks intruded by the foot wall granite which in turn is older than the norite. There is no evidence, therefore, that the micropegmatite and other silicates so generally present in the massive sulphides can be regarded as having formed contemporaneously with the sulphides from a common magma. These silicates are derived from rocks older than the sulphides.

The evidence found at Crean Hill and Victoria is in accord with these conclusions. At these deposits the country rocks are greenstones or hornblende schists. The ore is filled with inclusions, large and small, of these rocks, but granitic material and micropegmatite are notably absent.

CONCLUSIONS.

A slight but definite alteration of the ores subsequent to the original formation of the deposits introduces factors that place serious difficulties in the way of a satisfactory petrographical study. Nevertheless the evidence presented may properly be used in reaching certain general conclusions.

That the origin of the Creighton ore can not be attributed to metasomatic processes would seem to be proved conclusively by the common, intimate mixture of granite, greenstone, and norite fragments as inclusions in the sulphides throughout the ore-body.

On the other hand, although the evidence is less certain on account of the alteration of the rocks, it does not seem to corroborate the statements of those who advocate the magmatic origin of the ore that there is a gradation from norite to massive sulphide in a petrographical sense.

The field evidence as well as that obtained from thin sections strongly suggests, however, that the sulphides were originally introduced to their present positions in a molten condition. The brecciated character of the contacts between ore and country rock, as well as the fineness of grain of the norite close to the contact would seem to indicate that the sulphides were intruded after the norite had cooled, and that they represent, perhaps, an end product in the differentiation of the magma from which the norite was derived. In other words, the differentiation, of sulphides and

silicates at least, was effected in the magma reservoir and not in the laccolithic chamber.

As a result of their metallographic study of the Sudbury ores, Campbell and Knight[1] concluded that pyrrhotite was the first sulphide to form, probably from aqueous solution, that it was subsequently fractured, and that pentlandite and later chalcopyrite were deposited in the cracks. The relations are undoubtedly as Campbell and Knight have described them in so far as large masses of pyrrhotite are traversed by veins of pentlandite and chalcopyrite, but to the writer they would seem to be better explained by the nearly simultaneous cooling of the different sulphides that had previously separated as distinct mineral compounds, non-miscible, though still molten.

Igneous intrusion by the sulphides is essentially the explanation given by Coleman to account for certain of the "offset" deposits.[2] A similar explanation would appear to apply equally well to the most typical of the sulphide deposits in contact with the main norite mass, and, so applied, would relieve the theory of magmatic origin of the burden of many troublesome problems in physics and chemistry.

[1] *Op. cit.*, p. 365.

[2] Coleman, A. P., "The Nickel Industry," Canada, Dept. of Mines, Mines Branch, 35–38, 1913.

ON THE DEPOSITION OF GOLD IN NATURE.

VICTOR LENHER.

In a general survey of different studies which have been made on the genesis of gold deposits, the deposit of gold in hand is presumably considered to have been precipitated from a gold-bearing solution by means of a reducing agent. In other words, the studies on the transportation and deposition of gold in nature assume that gold is transported by a natural solvent and is deposited at the place where it is found by reduction of the gold from its soluble form to the metallic condition. The ease with which gold is precipitated from solutions by the various reducing agents is one of the striking characteristics of the chemistry of gold. The chemical inactivity of gold is so pronounced that even the mildest reducing agents have appeared to be the plausible substances which have caused its deposition in nature. The abundant sulphides, pyrite in particular, which are so commonly gold bearing, and the wide distribution of ferrous containing minerals and solutions, as well as the surface accumulations of deposits of organic matter have in turn been considered to be significant precipitants of gold. In general it may be said that the deposition of gold in nature has been explained largely by the precipitation of gold from solution by one of the numerous reducing agents which occur in nature.

On the other hand, very little attention has been directed to the precipitation of metallic gold from solution by oxidizing agents. The subject of "auto-reduction" has numerous examples in the broad field of chemistry, such as the mutual reduction of potassium permanganate and hydrogen peroxide when brought together, the reduction of iodates and hydrogen peroxide whe brought in contact, the mutual reduction of permanganate with either percarbonates or perborates. In all of these cases the mutual reduction of these oxidizing agents is accompanied by

the evolution of gaseous oxygen, the commonly given explanation being that both of the oxidizing substances lose atomic oxygen which unites to form molecular oxygen which is evolved in the reaction as oxygen gas.

A few cases of the "auto-reduction" of gold compounds are known, but the general principle of the deposition of gold in the ores by this means has not received systematic study.

It has long been known that when the oxide of gold or the oxide of silver is brought in contact with hydrogen peroxide, the hydrogen peroxide will reduce either of these oxides to metal, oxygen being evolved and water being formed simultaneously:

$$Au_2O_3 + 3H_2O_2 = 2Au + 3H_2O + 3O_2,$$
$$Ag_2O + H_2O_2 = 2Ag + H_2O + O_2.$$

Not only is the oxide of gold reduced to metal by means of hydrogen peroxide, but solutions of the gold compounds deport themselves similarly, gold being thrown out of solution when hydrogen peroxide is added. This precipitation takes place from either acid, neutral or alkaline solution.

Sodium peroxide, barium peroxide, and calcium peroxide when introduced into gold solutions precipitate metallic gold immediately. Sodium perborate deports itself in an entirely similar manner toward gold solutions, precipitating metallic gold at once. The chemical deportment of these peroxidized compounds in solution is in general similar to the behavior of an alkaline solution of hydrogen peroxide, and it is not surprising that they react with gold solutions in the manner that they do.

There are a number of peroxidized compounds that are not so closely related to hydrogen peroxide that deport themselves toward gold solutions as reducing agents through the same principle of auto-reduction. Osmium tetroxide, or the so-called osmic acid, when dissolved in water will not reduce gold solutions to metal, but when the free acid is neutralized or when the solution is made alkaline with sodium hydroxide, sodium carbonate or when neutralized with calcium carbonate gives metallic gold from a gold solution.

Nickel and cobalt yield peroxides when their solutions of their salts are treated with alkaline hypobromites. These peroxides of nickel and cobalt when brought in contact with a solution of gold which has been rendered alkaline cause precipitation of gold.

Lead dioxide as well as red lead precipitate metallic gold from either neutral or alkaline gold solutions.

Cerium dioxide, prepared in the hydrated form by precipitation from a ceric chloride solution by sodium hydroxide, precipitates metallic gold at once from a gold solution which has been rendered alkaline.

Along this same line of autoreduction the compounds of manganese behave in an interesting manner with gold solutions. Manganese dioxide prepared by the treatment of a manganese acetate solution with bromine precipitates gold from its solution either under neutral, alkaline, or slightly acid conditions. Similarly, when potassium permanganate is allowed to stand for some time with chloride of gold solution, metallic gold slowly separates out of the solution along with manganese dioxide.

Not only will artificially prepared manganese dioxide cause metallic gold to be deposited from gold solutions, but also the manganese oxide minerals deport themselves similarly. The minerals, pyrolusite, wad, braunite, and manganite slowly cause metallic gold to deposit on them when immersed in a gold solution which is either acid, alkaline or neutral.

This deposition or precipitation of metallic gold by these various oxidizing agents necessarily proceeds far more satisfactorily in most cases in alkaline solution. A neutralized solution with a number of the oxidizing agents is sufficient for the precipitation reactions to take place, but a material amount of free acid can not be present with the oxides of manganese, lead, nickel, cobalt, or cerium, as in acid solution the reaction takes the opposite direction, namely that of acting as a solvent for gold. For example, manganese dioxide with an appreciable amount of hydrochloric acid is a solvent for gold rather than a system from which it will readily deposit.

In the studies which Brokaw[1] has made with manganese compounds and gold solutions note is made of the precipitation of metallic gold by alkaline manganese solutions and by manganese carbonate. The explanation of these reactions by Brokaw is in the formation of minimal amounts of manganese tetrachloride which is hydrolyzed, removing the manganese from solution, and that this hydrolysis proceeds more efficiently by the neutralization of the free acid formed.

That manganese can be of considerable importance in the deposition of gold is very probable, but in addition to the suggested explanation a number of other chemical facts must be considered. Auric compounds, as is well known, are readily reduced to metallic gold, hence can be considered oxidizing agents in the ordinary sense of that term, and in alkaline solution can oxidize manganous hydroxide to manganese dioxide. Further, the neutralization or the rendering alkaline of a manganese solution brings into the system the omnipresent oxygen of the air which, as is well known, causes the deposition of manganese dioxide, which in turn is a precipitant for gold.

As a matter of fact, the manganese oxide deposits in nature are doubtless largely formed by the neutralization of manganese-bearing waters and the oxidation which proceeds simultaneously by the oxygen of the air. The facts that manganese dioxide is a precipitant for gold and that it is presumably largely formed by the oxygen of the air, lead to the conclusion that the real important agent in this precipitation of gold by manganese is the oxygen of the air. The system is undoubtedly complex, and the true direction of the reactions between manganese compounds and gold solutions depend largely on the acidity or alkalinity of the solutions and to the time factor, particularly in so far as the oxygen of the air is concerned.

The oxygen of the air is by no means necessary in the reaction between alkaline gold solutions and manganese salts as has been evidenced by the immediate precipitation of metallic gold and manganese dioxide when experiments were conducted in the

[1] *Journal of Engineering and Industrial Chemistry*, 5, 560, 1913, *Journal of Geology*, 21, 260, 1913.

absence of air or in the presence of carbon dioxide in solutions which had been boiled until air free. The mutual precipitation of gold and manganese dioxide by calcite cited by Brokaw is simply the neutralization of the acid liberated in the hydrolysis of the manganese salt when the oxidation of the manganese by the gold solutions results in the precipitation of both manganese dioxide and metallic gold. The reaction, however, is slow, and as it proceeds the action of the oxygen of the air comes into play and the deposit of manganese dioxide appears larger and larger as the time of the reaction proceeds. Indeed when a large excess of manganese chloride or sulphate is introduced into an open vessel with calcite and the solution largely diluted to cause the deposition to take place slowly, after several days the calcite is covered with a thick layer of manganese dioxide which contains only a very small amount of gold. When this experiment is repeated with a pure manganese solution and calcite, the formation of manganese dioxide on the calcite crystals and on the sides of the vessel proceeds in exactly the same manner, but the deposit obviously does not contain gold.

That these are the general directions of these reactions is further evidenced by the duplication of exactly the same character of phenomena by replacing the manganese solutions with cerium compounds. Cerous hydroxide precipitates metallic gold in alkaline solution; the cerium being at the same time oxidized to cerium dioxide.

Similarly when a piece of calcite is introduced into a solution of cerium chloride and gold chloride, as the acid liberated by the hydrolysis of the cerium salt is neutralized by the calcium carbonate, a deposit of cerium dioxide containing metallic gold begins to form on the calcite. As in the blank experiment with manganese, a pure cerous salt when dissolved in water to a dilute solution, a piece of calcite added and allowed to stand for several days develops a deposit of cerium dioxide on the calcite and on the walls of the vessel.

The presence of gold in the manganese deposits, which observation has been studied by Emmons,[1] may be due to the fact

[1] Emmons, *Transactions American Institute Mining Engineers*, 1910, 768.

that manganese is a significant agent in the superficial transportation of gold, but such is by no means necessarily the case. Several distinctly possible kinds of reactions may be going on. In one case a chloride solution containing free acid coming in contact with an oxidized manganese deposit will produce free chlorine or its equivalent. This chlorine containing solution can then dissolve gold and cause the production of a gold bearing manganese solution. This solution, as long as it contains free acid, is entirely permanent, but when it comes in contact with any neutralizing agency, such as, for example, a limestone, metallic gold and manganese dioxide, would be at once precipitated. This accords with experiments which have been reproduced in the laboratory, but which do not require as the precipitating agent such a reducing agent as ferrous sulphate, as indicated by Emmons, or other reducing agents as indicated by Wells.[1] On the other hand, the presence of gold in manganese deposits adjacent to other gold deposits may owe their gold content wholly to the fact that gold solutions in contact with manganese dioxide, yield metallic gold through the principle of auto-reduction that other peroxides show with gold solutions.

The principle of the auto-reduction of gold solutions to metallic gold has apparently thus far not been considered as an important geological factor in the secondary deposition of gold, but it is doubtless possible that in many instances one can conceive of the oxygen of the air as being the real agent which causes the gold to be reduced in the presence of a manganese or similar compound which acts as a catalytic agent.

[1] *Trans. American Institute of Mining Engineers*, 1910, 793.

GEOLOGY AND ORE DEPOSITS OF THE SAN FRANCISCO AND ADJACENT DISTRICTS, UTAH.[1]

B. S. BUTLER.[2]

PART II.—ORE DEPOSITS.

GENERAL RELATIONS.

The ore deposits of the San Francisco region are believed to be of essentially the same age, the deposition of all the ores closely following the intrusion of the quartz monzonite. The marked differences in the deposits are probably due to several factors, among the more important of which are (1) differences in the character of the rock in which the deposits were formed; (2) the distance from the intrusive body, which affected the temperature, pressure, etc.; and (3) the time in the general period of mineralization in which the deposits were formed, the solutions in the later part of the period probably being of somewhat different composition from those that were active when mineralization began.

The character of the rock in which the deposits were formed was doubtless one of the more important factors in determining the general type of the deposit, and on this basis a classification of the deposits can be made that is convenient for the purpose of description and that groups deposits having a general similarity.

Under this classification the deposits of the region may be divided into three general groups—(1) deposits in the quartz

[1] Published by permission of the Director of the U. S. Geological Survey.

[2] This paper is a summary of the results of a study of the San Francisco and adjacent districts, Utah, which is presented in detail in Professional Paper No. 80, U. S. Geological Survey. The summary, prepared at the request of the editor, is intended to present in a concise form the features of more or less general interest. Those who have a particular interest in the districts or wish more details concerning any of the features presented, references to the literature, etc., are recommended to the complete report.

monzonite; (2) deposits in the sedimentary rocks; (3) deposits in the lava flows.

Deposits in the Quartz Monzonite.

The quartz monzonite has been mineralized at numerous localities in the region, but so far the mineralization has been shown to be extensive at only two places—in the Cactus ore zone, in Copper Gulch, and in the O K ore zone, in the Beaver Lake district. The deposits of this type are characteristically copper deposits with some gold and silver, though veins carrying galena have been opened in the quartz monzonite.

In both instances the deposits are associated with fractures along which there has been a brecciation of the rock but probably not extensive displacement. The deposits are more or less "chimney" shaped, this being especially true of the O K deposit which consists of a central "chimney" of pegmatitic quartz surrounded by altered and mineralized quartz monzonite (see Fig. 124).

In the Cactus zone the ore and gangue minerals are deposited in spaces between corroded fragments of the quartz monzonite. In both instances the structural relations indicate that the spaces occupied by the ore and gangue minerals were not formed principally by dynamic movement but that they resulted largely from the solution of the rock in the early stages of mineralization and the subsequent filling of the spaces thus formed. In the case of the O K deposit the solutions were apparently relatively confined and the dissolving action was strong resulting in the formation of a more or less cylindrical channel with a maximum dimension of fully 100 feet.

The change in the quartz monzonite adjacent to these channels has already been discussed and need not be repeated further than to say that it resulted in a sericitization and silicification and the addition of sulphides.

In the O K deposit the main channel is filled with coarse quartz individual crystals having a diameter of 10 inches and a length of 2 feet. The body as a whole has a striking resemblance to a

coarse pegmatite though no feldspar or mica are present. Usually sulphides are not abundant in the main "chimney" though locally, as in the ore body on the second level, they are abundant and by enrichment high grade ore has resulted. In the small veins of quartz extending from the main mass into the adjacent rock sulphides are much more abundant. The characteristic primary

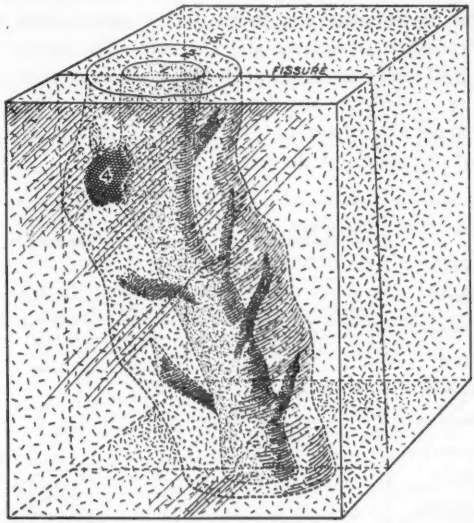


FIG. 124. Generalized stereogram showing the relation of pegmatitic quartz and altered and mineralized quartz monzonite in the O K mine. 1, pipe of pegmatitic quartz; 2, altered quartz monzonite; 3, quartz monzonite; 4, high grade ore.

minerals in the O K deposit are quartz, chalcopyrite, pyrite, and molybdenite, the latter in relatively small amounts.

In addition to the above characteristic occurrences there is an aplitic rock, probably a dike, exposed in the bottom of the shaft which contains chalcopyrite and molybdenite apparently as original constitutents.

In the Cactus ore zone in addition to the mineral mentioned

above, hematite, magnetite? tourmaline, siderite, anhydrite, and barite are present in important amounts.

The minerals in this deposit show a rather definite sequence of deposition as follows: The earliest effect of the ore solutions was the sericitization of the quartz monzonite and the deposition of quartz chalcopyrite and pyrite with small amounts of hematite and tourmaline in the wall rock. This was followed by the deposition of hematite and tourmaline together with the continued deposition of quartz and the sulphides mainly in open spaces. Still later deposition in the open spaces consisted mainly of siderite, anhydrite, and barite together with the sulphides. The accompanying diagram (Fig. 125) illustrates the relative periods of deposition of the several minerals.

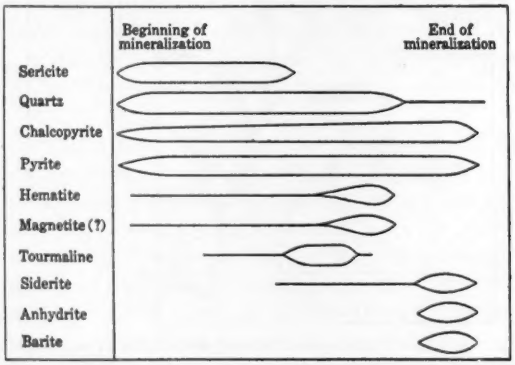


FIG. 125. Diagram showing the relative period of formation of the principal ore and gangue minerals of the Cactus ore zone.

It will be noted that the earlier mineralization of the Cactus zone was similar to that of the O K zone and the final difference in the two may be due to the fact that the Cactus zone underwent a longer and more varied period of mineralization. The later minerals are in general those that form under conditions of less heat and pressure and the succession of minerals might naturally be attributed to a gradual reduction of the heat and

pressure in the zone. Opposed to this hypothesis, however, is the fact that anhydrite, as opposed to most salts, decreases in solubility with increase in temperature and naturally would not precipitate from a cooling solution. To account for its presence Lindgren[1] has suggested the following explanation:

> "It is suggested as a possibility that during the later part of mineralization the anhydrite was precipitated by a reaction between ascending solutions of sodium sulphate and descending solutions containing calcium carbonate."

Too little is known concerning the behavior of anhydrite in complex solutions under considerable pressure to warrant any very positive statement concerning the conditions under which it was deposited.

Deposits Formed by the Replacement of Sedimentary Rocks.

The deposits occurring as replacements of sedimentary rocks may be separated into two types—contact deposits and replacement fissure deposits. In their typical development these types are readily recognized, but there are all gradations between the two.

Contact Deposits.—The typical contact deposits occur as replacements of the limestone near the quartz monzonite. This zone of replacement is extremely variable in size and also in character. Usually it consists largely of lime and magnesian silicates with variable amounts of sulphides but may be largely magnetite as at the Old Hickory mine. The general character of the alteration of the limestone has already been discussed.

The primary ores in these zones are low grade and, except in the magnetite zones, have been little mined, the production coming mainly from the oxidized zone. The deposits are characteristically copper deposits though other metals are present and iron may form on important commercial constituent.

Replacement Fissure Deposits.—The second type of replacement deposits consists of replacements of the sedimentary rocks

[1] Lindgren, Waldemar, "Anhydrite as a Gangue Mineral," ECON. GEOL., Vol. 5, 1910, p. 522.

along fissures. In the massive limestone deposits the replacement may occur rather uniformly in different beds, producing locally a roughly tabular deposit parallel with the fissure. Where the sediments are of varying physical character and chemical composition, however, the ore deposition has extended out from the fissure in certain beds for considerable distances, though adjacent beds have suffered little if any replacement by the ore minerals. This selective replacement of the beds is probably due in part to differences in the physical character of the beds and in part to differences in chemical composition.

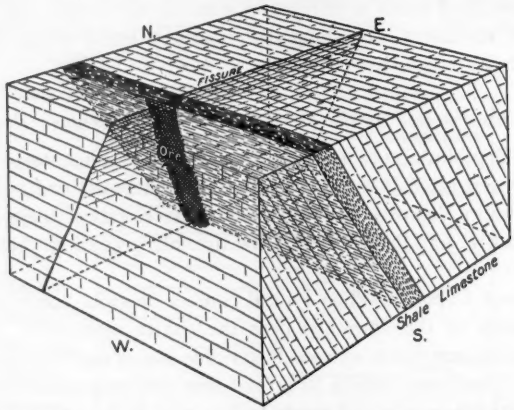


FIG. 126. Stereogram showing ore shoot beneath shale. The shoot follows the intersection of the ore fissure and the limestone bed beneath the shale. The ore makes out from the fissure along the limestone bed.

The tabular development is perhaps best shown in the Mammoth mine. This deposit is in the massive Topache limestone, and though it shows a pronounced swelling or extension into some of the beds the intervening beds also have been replaced to a considerable extent. The replacement along certain beds is well shown in the Harrington-Hickory mine and in the mines underlying the Mowitza shale, especially the Red Warrior and Moscow. In these deposits the replacement has been effected

almost exclusively along certain beds, the resultant deposits forming "chimneys" following the intersection of the ore fissure and the replaced bed (see Fig. 126). In the deposits underlying the Mowitza shale the reason for this selective deposition seems to be largely physical. Where the fissures pass through the shale the character of this rock has caused them to be "tight" and relatively impervious to the passage of solutions. The ore-bearing solutions, rising along the fissures till they came to this zone, were forced to spread out under the shale and thus replaced the more permeable beds underlying it. A similar formation of ore bodies beneath shale beds has been noted in several localities in the west.

In the Harrington-Hickory mine the chemical composition of the beds has undoubtedly had an influence on the form of the deposit. The series is made up of interbedded limestone, quartzite, and siliceous shales and limestones. The main ore deposition has been in the limestone, the siliceous beds being very slightly replaced, and though the physical character of the beds may have had some effect on the deposition it is thought that the chemical composition was the controlling factor.

The characteristic alteration of the limestone adjacent to the fissures is silicification.

The most important metals of this class of deposits are lead and silver, though they contain varying amounts of zinc and copper. The deposits have undergone extensive secondary alteration.

Transition Type.—Deposits that may be considered as constituting a transition type are formed as a replacement of limestone along fissures, like the replacement fissure deposits, but the alteration of the wall rock has resulted in the formation of minerals similar to those occurring in the contact deposits, namely, garnet, magnetite, fluorite, muscovite, etc. These deposits occur at no great distance from the igneous rock. Such deposits are present in the Wild Bill and Hub mines, where, in fact, they merge into true contact deposits. The Harrington-Hickory and Moscow mines may also be considered of this type, for they contain con-

tact minerals in considerable amount, but as contrasted with the Wild Bill and Hub mines they approach the replacement-fissure type rather than the contact type. Though the replacement deposits in sediments are confined mainly to the limestones or highly calcareous sediments, some ore occurs as a replacement of quartzite, the general relations being similar to those of the deposits in limestone.

Mineralization in the Lava Flows.

The mineralization in the volcanic rocks that to the present time has been shown to be of commercial importance is confined to two deposits on the eastern flank of the San Francisco Range—the Horn Silver and the Beaver Carbonate. Mineralization in the lavas has taken place elsewhere, however, and it is possible that other deposits of commercial value exist.

The deposits are of the type known as replacement fissure veins in which the ore and gangue minerals in part filled open fissures and in part replaced the brecciated rock adjacent to the fissures. In the Horn Silver deposit the ores occur in and adjacent to a strong north-south fault that has a displacement exceeding 1,600 feet. In the Beaver Carbonate deposit the mineralization has occurred along an east-west fault of undetermined displacement.

The alteration of the wall rock adjacent to these deposits shows considerable variation. In the Horn Silver deposit the less intense alteration consists of a sericitization of the lavas while where the alteration has been most complete the rock is changed to a mass of finely crystalline quartz containing rather abundant pyrite and some barite. The almost complete silicification of the rock may extend for 100 to 125 feet from the fissure and where the ore bodies fail in depth their downward extension is represented by the silicified rock (see Fig. 129 p. 552).

The limestone which forms the footwall of the deposit has been but slightly silicified. The alteration seems to have affected mainly the permeable brecciated lavas while the massive limestone has been little changed.

The wall rock of the Beaver Carbonate mine shows much less intense alteration than those of the Horn Silver—the hornblende has been chloritized while the plagioclase has been partially sericitized. Orthoclase and biotite show little alteration.

Ore Minerals of the Deposits in Lava.—In the Horn Silver deposit the principal primary ore minerals are galena, pyrite, and sphalerite, with lesser amounts of sulphantimonides and sulpharsenides. The ore minerals occur almost entirely as a replacement of the volcanic rocks and the different minerals are believed to be essentially contemporaneous in origin. The important primary gangue minerals are quartz, barite, and the altered country rock.

In the Beaver Carbonate mine the primary ore minerals are galena, pyrite, and sphalerite, and the principal gangue minerals are carbonate and quartz, together with the altered country rock. These minerals are disseminated through the altered rock and fill open spaces between the breccia fragments. The minerals forming in the open spaces are fine cherty quartz, sulphides, and calcite, deposited in general in the order named. The periods of deposition are not sharply defined, however, as some sulphide was deposited with the quartz, some calcite with the sulphides, and a little quartz with the calcite.

GENESIS OF THE ORES.

As has already been indicated it is believed that the ore deposits of the region were all formed during the same general period of mineralization and that they had a common origin. This common origin as indicated by similarity of composition of the solutions effecting the alteration in the ore zones in the quartz monzonite and the contact zones in the limestone has already been discussed. That the solutions forming the replacement fissure deposits in sedimentary rock had a common origin with those that formed the contact deposits is amply indicated by the gradation from the one to the other.

That the solutions affecting the rocks at different points were exactly the same does not seem probable. As the solutions tra-

verse the rock they are constantly taking up and depositing material so that it may be imagined that a solution deficient in one element at a given point may be rich in that element farther on its course or the reverse may be true. Differences in the character of the rock and also in the physical conditions, as temperature, pressure, etc., may also be important factors. For example, the solutions forming the contact zones deposited copper and iron sulphides but only small amounts of lead and zinc sulphides. In the replacement fissure deposits, farther from the intrusive mass and under conditions of less heat and pressure lead and zinc were deposited.

The relations of the deposits in the lava to the others is less clearly shown. The general relations of the deposits, however, strongly suggest their connection with the quartz monzonite body. The Horn Silver deposit is in the direction of the long point extending out from the main body of quartz monzonite and the intrusive rock is said to reach the Horn Silver fault on the 11th level of the mine. The Beaver Carbonate mine is also in line with the eastward extension of the quartz monzonite body and the fissures may logically be supposed to reach that rock at depth, in fact it seems highly probable that the fissuring was the result of the intrusion. These relations, while by no means conclusive, certainly suggest a genetic connection. Such a connection for similar deposits is also shown in the Marysvale district to the east.[1]

The origin of the ore-bearing solutions is not susceptible of positive proof but certain facts indicate that the quartz monzonite magma was the original source.

In seeking for the origin of the solutions two general sources may be considered, namely, meteoric waters circulating through the rocks and collecting their metal content and waters given off by the crystallizing igneous magma containing the metallic elements in solution. That waters and metallic deposits are derived from both these sources is too well known and has been too frequently discussed to make it necessary or desirable to treat it in detail in this place.

[1] Butler, B. S., and Gale, H. S., "Alunite, a Newly Discovered Deposit near Marysvale, Utah," U. S. Geol. Survey Bull. 511, 1911.

It is certain that the solutions forming the deposits were hot as shown by the character of the mineral. These solutions may have been given off by the magma or they may have resulted from the heating of metoric waters that came into proximity with the intruded rock or they may have been furnished from both these sources.

In seeking to determine which of these sources has furnished the solutions or which has been dominant we may first discuss the deposits in the quartz monzonite.

As has been noted in the section on petrography, the quartz monzonite contains aplitic dikes composed principally of quartz and feldspar, and the composition and relations of these dikes indicate that they are the siliceous differentiation products of the quartz monzonite. In the bottom of the O K shaft what appears to be an aplitic dike contains chalcopyrite and molybdenite as original constituents of the rock, thus seeming to indicate that the sulphides were relatively abundant in the siliceous differentiation product of the magma. In the same mine the "chimney" of quartz with sulphides of copper and molybdenum, which forms the "ore channel," has every appearance of a coarse pegmatite, and it seems reasonable and logical to consider this a further stage in the differentiation of the quartz monzonite magma. As the same solutions that carried and deposited the pegmatitic quartz undoubtedly deposited the ore minerals in this quartz and altered the surrounding rock and deposited the sulphides in it we are led to the conclusion that these solutions were derived from a differentiation of the quartz monzonite magma.

The similarity of the Cactus deposit to that of the O K mine leaves no room for doubt that the solutions had a similar origin, though they passed through a more varied cycle of physical conditions, the later minerals of the Cactus deposit not having been formed in the O K deposit. Moreover, the presence of tourmaline and copper minerals intimately associated with an aplitic dike on Black Mountain, south of the Cactus deposit, point to the same conclusions concerning the origin of the solutions for this as for the O K deposit.

That the ores were deposited during the general period of igneous activity of which the intrusion of quartz monzonite is one phase, is indicated by the presence of dikes of kersantite cutting the ore body of the Cactus mine. These dikes are believed to represent a late stage in the differentiation, probably closely following the deposition of the ores.

The evidence as to the origin of the solutions that produced the deposits in the sedimentary rocks is most conclusive for the contact deposits. The very close association of the contact ores with the quartz monzonite is in itself suggestive of genetic relation. At the immediate contact at some points there is a blending of the quartz monzonite and the altered limestone so that there is a transition from a group of minerals characteristic of the one to those characteristic of the other. It is believed that this condition is most readily explained by assuming that the altering solutions were given off by the igneous body. It is most natural to extend this explanation to the formation of similar deposits where the relation is less close and the solutions may have been of a deeper seated origin. Further, small fissures that were opened in the altered limestone probably soon after the intrusion as a result of the readjustment of stresses, contain veinlets or dikelets composed of quartz, feldspar, magnetite, and sulphides. These do not differ greatly in composition from the aplitic dikes in the quartz monzonite, and it is most natural to suppose that they had a similar origin—that is, that they were a differentiation from the quartz monzonite magma. The composition of these veinlets indicating the giving off of solutions competent to effect the alteration of the limestones as it exists. The similarity in the composition of the solutions that effected the alteration in the quartz monzonite and in the limestone also points to a common origin.

The close relation between the different types of deposit in the sedimentary rocks indicates a similar origin for each type. It is entirely possible, however, that meteoric waters may have played some part in the formation of the deposits at a distance from the intrusive body. It is, however, thought that the metal content of all the deposits was derived from the quartz monzonite magma.

These conclusions agree in general with those arrived at by others in the study of similar deposits; in fact, it may seem to some that it is no longer necessary to give detailed evidence to substantiate such conclusions.

In metal constituents the deposits in the lava flows are similar to the replacement fissure deposits in limestone, both types being characteristically lead-silver-zinc-copper ores with very little gold. The general relations of the ore deposits in the lava to the intrusive rock suggest a derivation from the quartz monzonite magma and this agrees with observations in other districts, but such an origin for the deposits in this region has not been positively demonstrated.

ALTERATION OF ORES.

GENERAL CONDITIONS.

The change produced in the mineral deposits of this region by the action of surface solutions has been an important though variable element in the production of the ore deposits as they now exist. It is a striking fact that some of the deposits have been but little affected by such alteration, whereas the character of neighboring deposits has been completely changed. The region is in some respects especially favorable for a study of certain features of the problem of secondary alteration, and this will be discussed in some detail.

The secondary alteration has been dependent on several factors, among the more important of which are the position of the ground-water table, the rapidity of erosion, the physical character of the deposit, and the mineral composition of the deposit. All these factors have doubtless had some effect in all the deposits, but in several of the deposits some one of them seems to have exerted a dominant influence.

Water Level.

In general it may be said that the position of the ground-water level has been an important factor in determining the extent of secondary alteration in the ore bodies, for extensive alteration has

probably not extended very far below this level, though if given sufficient time it would reach this level regardless of other conditions. Other factors have been of great importance, however, in determining the rate at which alteration has proceeded.

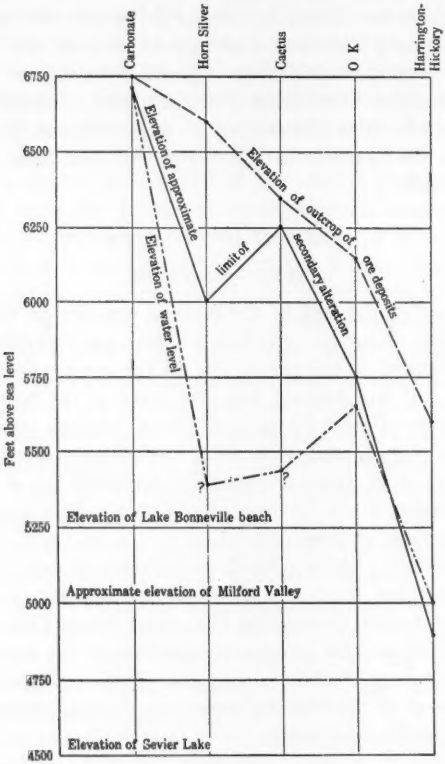


FIG. 127. Diagram showing the relation of secondary alteration to outcrop of ore body and to water level.

In but few of the mines of the district has the water level been determined. The accompanying diagram (Fig. 127) shows the

elevation above sea level of the outcrop of several of the deposits, the lower limit of important secondary alteration, and the approximate ground-water level. The upper limit of ground water is shown in the figure, but the actual position may be considerably lower.

It is not likely that the water level has remained constant for long periods in the past. In fact, there are good reasons for believing that it has been both higher and lower than it is now. The beaches of the old Lake Bonneville are about 750 feet above the present surface of Sevier Lake, and because of the more humid climate prevailing at that time it is reasonable to suppose that the water level throughout the region was considerably higher than at present. On the other hand, the great alluvial cones at the mouths of the valleys upon the Bonneville beaches were deposited testify to a long period of aridity preceding the Lake Bonneville epoch, and it is not unlikely that at that time the water level was lower than at present.

The inability to determine the position of the water level in the past makes it impossible to determine accurately the relation of the water level to secondary alteration, but it is practically certain that in some of the deposits secondary alteration has never reached the ground-water level even in its highest stages. This is especially true of the Cactus mine, where the water level in Lake Bonneville time must have been considerably below the present zone of alteration, and it is doubtless true of the Horn Silver mine. On the other hand, at the Harrington-Hickory mine oxidized ores are present on the sixth level, 100 feet below the present position of the ground water, indicating a lower water level at an earlier period.

The Carbonate mine is the only one in the region where the present water level and the zone of oxidation show a close relation. In that mine the water level is but slightly below the surface, and this has prevented any extensive alteration of the ore body.

Rapidity of Erosion.

The rate at which the surface is lowered by erosional agencies may be an important factor in determining the extent of the zone of alteration, for if erosion is sufficiently active the altered rock may be removed almost as rapidly as it is formed. There is little doubt that erosion is lowering the surface in the San Francisco Range more rapidly than in some other parts of the area. From this it is to be expected that the zone of alteration will be thinner in the San Francisco Range than, for instance, in the Beaver Lake Range, and comparison of the very similar Cactus and O K deposits proves this to be the case. As will be shown later, however, it is thought that the shallowness of the zone of alteration in the Cactus mine is due in part, possibly in large part, to causes other than rapid erosion, although its situation in the bottom of Copper Gulch is favorable to rapid erosion.

Effect of Physical Character of Deposits.

It is readily apparent that the physical character of a deposit will have an important influence on the rate at which it will yield to secondary alteration. A massive, dense deposit or one for some other reason relatively impervious to solutions must necessarily alter more slowly than an open, porous one, other conditions being equal. As examples of this difference may be cited the massive garnetiferous deposits like that of the Imperial mine, which have suffered but relatively superficial alteration, and the more open fissure deposits like some of those in the Star district, which have been altered for at least several hundred feet below the outcrop. The influence of the physical condition, however, may be offset by other factors, as in the Cactus deposit, which although open and readily permeable has been but superficially altered.

Effect of Mineralogic Character of Deposits.

The mineralogic character of a deposit may be an important factor in determining the rate at which secondary alteration will take place and also the character of such alteration. As the results

are very different in different deposits and are of interest not only mineralogically but also commercially, they will be discussed in some detail. In this discussion the alteration in the different types of deposit will be considered separately.

ALTERATION OF COPPER DEPOSITS IN QUARTZ MONZONITE.

The alteration of the ore bodies in the two principal deposits in the quartz monzonite may be briefly summarized as follows:

In the O K deposit, to a depth of fully 200 feet, the sulphides, pyrite and chalcopyrite, have been altered mainly to hydrous iron oxide with a relatively small amount of copper carbonates, except in the lower part of the zone where the carbonates become more abundant. Underlying this zone of hydrous iron oxide was a zone of enriched sulphides consisting of covellite and chalcocite replacing chalcopyrite and pyrite. Beneath the enriched sulphide zone are primary sulphides.

In the Cactus mine there is a shallow zone in which the sulphides have been altered to hydrous oxides of iron and carbonates of copper, the copper minerals being relatively abundant and the ore showing little loss in copper content. Directly beneath the zone of oxide and carbonate are primary sulphides. No enriched sulphides are present in the deposit.

There seems to be nothing in the physical character of the deposit or in the position of the water table to account for this difference. The relative shallowness of the zone of oxides and carbonates in the one case might be explained by the more rapid erosion of the outcrop of the Cactus deposit, but this in no wise explains the absence of enriched sulphides. It seems then that the cause for the differences must be sought in the mineral composition of the ores, and this seems to furnish an adequate explanation.

The minerals of the O K deposit are mainly chalcopyrite and pyrite in a gangue of quartz and muscovite (sericite). In addition to these minerals the Cactus deposit contains important amounts of carbonate (calcium, magnesium, iron, manganese carbonate), hematite, tourmaline, and lesser amounts of anhydrite

and barite. There is no reason for believing that the hematite, tourmaline, anhydrite, or barite have effected notably the alteration products resulting from oxidation of the sulphides. The carbonate, however, seems to have been an important factor.

In the O K deposit the alteration may be assumed to have taken place in the generally acepted manner, namely, pyrite was oxidized to sulphuric acid and ferrous sulphate and chalcopyrite underwent a similar change to cuprous and ferrous sulphate. The ferrous sulphate upon further oxidation would yield ferric sulphate, which in turn would form hydrous oxide and sulphuric acid. The acids thus formed assisted in the further oxidation of the sulphide. The copper sulphate together with iron sulphate would be carried to lower portions of the ore body and the reducing effect of the sulphides on the solution would cause the precipitation of the copper and form the zone of enriched sulphides. In the case of the Cactus deposit the sulphuric acid resulting from oxidation of pyrite would react with the carbonate gangue to form sulphates of lime, magnesia and iron. The relatively stable lime and magnesia sulphates would be deposited or carried out of the ore zone, while the iron sulphate would in turn break down, as already indicated. This process would result in the removal of the acid radical in the oxidation process since it would be either deposited as sulphate or removed in solution. The copper sulphate would also react with the carbonate yielding copper carbonate and sulphates. The relatively stable copper carbonate would remain in the oxidation zone and there would be slight migration of copper and no opportunity, while the carbonate was abundant, for the copper sulphate solutions to pass to the zone where the copper content would be deposited as sulphide. It seems, therefore, that the abundant carbonate gangue has been the controlling factor in preventing the formation of a zone of enriched sulphide in the Cactus deposit.

ALTERATION OF THE CONTACT DEPOSITS.

The oxidation zone in the contact deposits has generally been relatively shallow and consists commonly in the formation of

carbonates and hydrous oxides with varying amounts of secondary sulphides. The oxidation has apparently proceeded in a manner similar to that outlined above. Where calcite was an important gangue mineral carbonates have resulted; where the contact silicates were the main gangue there has been a downward migration of copper and the formation of enriched sulphides. In the subsequent oxidation of the enriched sulphides the oxide of copper is a common product. Much of the ore thus far extracted from the contact zones has been considerably enriched by these secondary processes.

ALTERATION OF REPLACEMENT FISSURE DEPOSITS IN SEDIMENTARY ROCKS.

The replacement fissure deposits have undergone extensive alteration and in but relatively few places in the area are the primary ores exposed.

So far as can be judged from the limited opportunities of observation the primary mineralization consisted of sulphides of lead, zinc, iron, and copper in varying proportions in a gangue of calcite and quartz with "contact" silicates in some instances.

The oxidized ore minerals are mainly limonite, cerusite, and small amounts of copper and zinc usually as the carbonates. Sulphates are present in relatively small amounts, including anglesite and the more complex sulphates jarosite and plumbojarosite.

The change that has taken place has been essentially as follows: Galena has, in some instances, and probably commonly, first altered to anglesite and later to cerusite, the latter being the common lead mineral of oxidized ore. To some extent iron and lead are combined in the complex sulphate plumbojarosite. Pyrite has altered to limonite and chalcopyrite to limonite and copper carbonate. In some places jarosite has apparently been an intermediate product between iron sulphide and limonite. Zinc is present to a limited extent in the oxidized ores as smithsonite and calamine, but has been largely removed from the upper portion of the ore body.

In general it may be said that there has been but slight migra-

tion of lead, iron, and copper, while sulphur and zinc have been largely removed. It is possible that the zinc has been deposited at greater depth as carbonate and silicate, though present developments do not furnish conclusive evidence on this important point.

ALTERATION OF DEPOSITS IN LAVA FLOWS.

The Horn Silver and Beaver Carbonate mines are the two important deposits thus far developed within the lava flows. The water table at the Beaver Carbonate mine is but a short distance below the surface and there has been but comparatively slight alteration. In the Horn Silver deposit the water table is deep and alteration has been an important factor in producing the ore body as it now exists. The following discussion will be confined to that deposit.

For the purpose of description, the deposit may be divided into the three zones commonly recognized in copper deposits that have been altered, namely the oxidized zone, including the portion composed mainly of oxides, carbonates, and sulphates; the enriched sulphide zone, including the portion which contains important amounts of sulphides deposited from downward moving solutions; and the primary zone in which the minerals are present essentially as orginally deposited by ascending solutions.

Primary Zone.—The important primary minerals of the main ore body are galena, sphalerite, and pyrite, with small amounts of jamesonite or some closely allied mineral, chalcopyrite and possibly other copper minerals, argentite and pyrargyrite or some mineral closely allied to it.

There are some relatively small bodies (notably to the north of the main shoot on the seventh level) in which the primary mineralization consisted mainly of pyrite with small amounts of the other minerals.

Enriched Sulphide Zone.—The enriched sulphide zone is characterized by the secondary copper minerals, covellite and chalcocite, and the zinc sulphide wurtzite, together with the primary minerals in variable amounts.

Oxidized Zone.—In the oxidized zone the recognized lead

minerals are anglesite, cerusite, plumbojarosite, beaverite, linarite, and bindheimite. Zinc occurs as smithsonite, calamine, and goslarite. The copper minerals are brochantite, malachite, azurite, chrysocolla, and chalcanthite, and the lead copper minerals mentioned. Cerargyrite was the only important secondary silver mineral observed. Hydrous oxide of iron and manganese are present in the oxidized ores.

The characteristic features of the oxidized zone are the great predominance of sulphates, the small amount of oxidized zinc ore, and the small amount of oxidized copper ore, except immediately above the secondary sulphide ore.

The formation of the ores of the oxidized zone is susceptible of the following general explanation. It is recognized that the process must have been more complex in detail. Galena when acted on by surface waters was altered to anglesite, this mineral is relatively insoluble and there was little migration of the lead. To a slight extent the anglesite was subsequently altered to cerusite but this was not important as indicated by the following analysis by S. B. Newberry[1] of a representative sample of the ores from the upper levels.

ANALYSIS OF HORN SILVER ORE NO. 1.

	Per Cent.
Moisture	Undetermined.
Silica	15.17
Sulphate of barium	.49
Sulphate of lead	74.51
Sesquioxide of iron	4.80
Sesquioxide of alumina	1.71
Sulphide of antimony	.37
Sulphide of arsenic	1.12
Lime and magnesia	.50
Carbonic acid	.62
Silver (by fire assay, 78.33 [ounces] per ton).	
	99.62

"No zinc was found; the quantity is certainly very small and did not show itself, although a special determination was made to ascertain it. The metallic lead, arsenic, and antimony in the ore are as follows: Lead, 50.90 per cent.; arsenic, 0.93 per cent.; antimony, 0.26 per cent. The amount of moisture in the ore is very small, the average of the run-of-mine being less than 3.5 per cent., and the sample analyzed above had been thoroughly dried."

[1] Report to the Horn Silver Mining Company, by W. A. Hooker, 1879.

To a relatively slight extent lead entered the complex sulphates, beaverite and plumbojarosite.

Sphalerite was likewise oxidized to the sulphate and this highly soluble material was largely removed from the oxidized zone. The movement of the zinc is amply exemplified at the present time in the lower levels of the mine where the surfaces of zinc ore are frequently covered with festoons of goslarite. To a slight extent smithsonite and calamine were formed and remained in the oxidized zone.

The copper minerals observed in the zone of oxidation were formed from the alteration of the rich sulphide ores. The chalcocite and covellite have altered to brochantite, which is the important copper mineral of the zone. This mineral apparently commonly alters in turn to the soluble sulphate which is carried out of the zone and thus the oxidized copper ores are kept close to the sulphides. To a slight extent the brochantite alters to carbonate and silicate, but these are apparently eventually acted on by acid solutions and the copper removed, as indicated by their scarcity in the upper parts of the ore body.

The silver contained in the argentiferous galena and in other silver-bearing minerals commonly altered to cerargyrite. There was evidently sufficient chlorine in the waters, probably derived from the salts of the desert, to combine with the silver. As the silver chloride is but slightly soluble, there has been little migration of silver.

Pyrite has probably undergone the normal alteration to ferrous sulphate and sulphuric acid. The ferrous sulphate in part may have altered to ferric sulphate and eventually to limonite and sulphuric acid. In part ferric sulphate evidently combined with other metals to form the relatively insoluble basic ferric sulphates. These, however, eventually broke down and limonite may have been a resulting product. Much of the iron has been removed probably as the sulphate. This removal is especially evident where argenitiferous pyrite has been altered, the resultant rock being a cellular mass in which the cavities retain the form of the altered pyrite crystals.

In the zone of sulphide enrichment the copper minerals have

formed as a replacement of pyrite, sphalerite, wurtzite, and galena. The copper entered the zone as sulphate that was derived from the alteration of copper minerals above and the zinc and iron sulphates formed by the reaction of the copper sulphate with the sulphides have evidently migrated to some distance; the lead sulphate on the other hand has apparently remained very close to its place of formation and it is probable that some of the lead sulphate of the higher zone has been formed in this manner rather than by the simple oxidation of galena. It is equally probable

FIG. 128. Covellite Replacing Zinc Sulphides, Horn Silver Mine. Zinc sulphides in the center, surrounded by zone of covellite containing considerable unreplaced zinc sulphide. Specimen collected by D. P. Rolfing.

that the alteration of some of the sphalerite and pyrite was accomplished in this manner rather than by simple oxidation.

In this zone the zinc minerals are sphalerite and wurtzite which show the following relations: The rich zinc ores are those in which wurtzite is relatively abundant; these rich ores are largely confined to breccia zones associated with faults (see Fig. 128). Very commonly the wurtzite surrounds centers of sphalerite or fills spaces between sphalerite grains (see Figs. 129 and 130). These relations suggest that the zinc sulphate solutions working

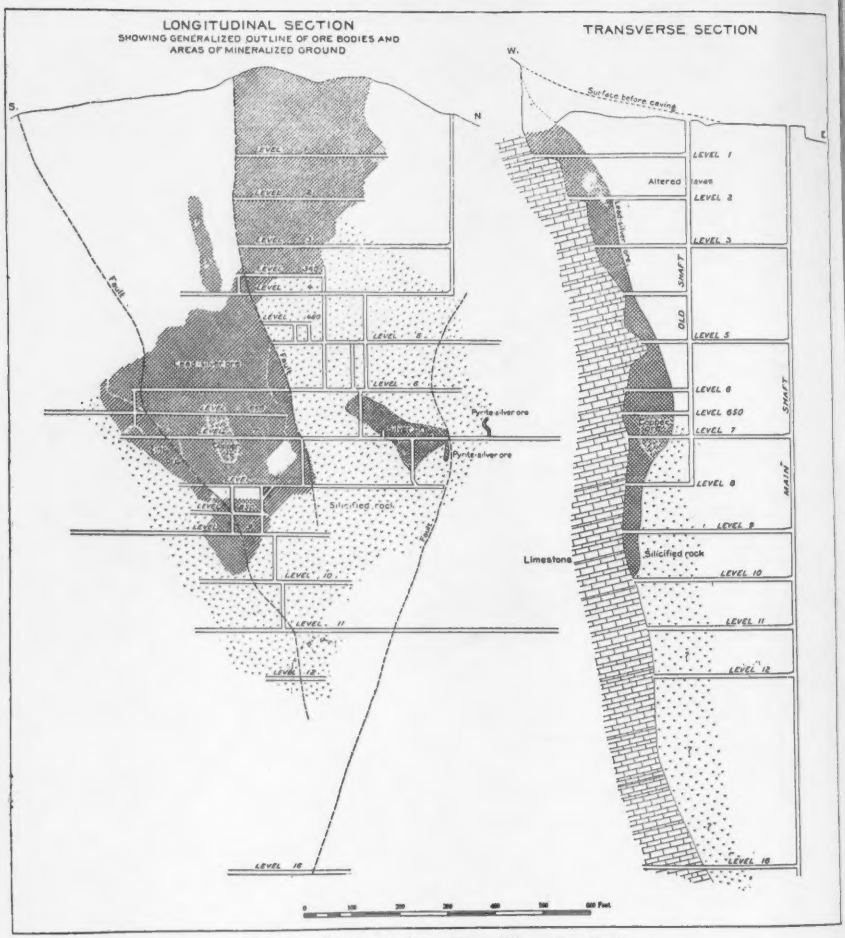


FIG. 129. Sections of the Horn Silver Ore Body.

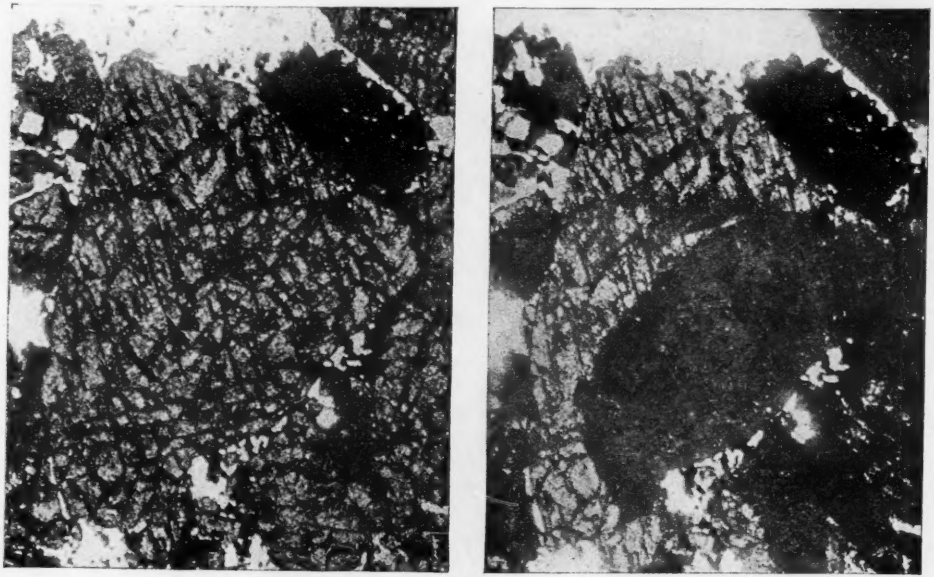


FIG. 851. Zinc Sulphides, Horn Silver Mine. A, Dark gray zinc sulphides, sphalerite and wurtzite; ordinary light; enlarged 43 diameters. B, Same specimen as A, with crossed nicols; dark areas, sphalerite, light gray areas, wurtzite. C, Crystals of zinc sulphides, ordinary light. Enlarged 43 diameters. D, Same as C, with crossed nicols; light areas, wurtzite surrounding a center of sphalerite.

downward along the more open channels, namely the brecciated areas, deposited their zinc content around the sphalerite grains. The crystallographic characters of the two sulphides of zinc are very similar and it seems probable that the sphalerite has controlled the crystallization of the wurtzite in many cases and resulted in the growth of wurtzite around the centers of sphalerite. No example of any sulphide being replaced by wurtzite has been noted and it therefore seems likely that the formation is not

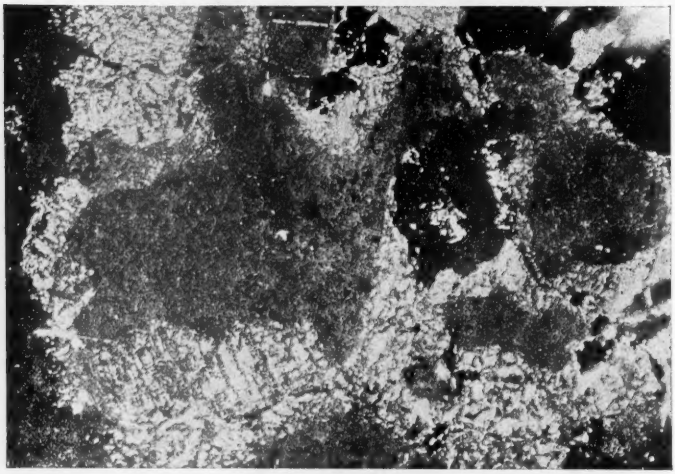


FIG. 852. Zinc Sulphides, Horn Silver Mine. Crossed nicols. Light areas, wurtzite, gray areas, sphalerite. Enlarged 43 diameters.

comparable to the formation of covellite as a replacement of sphalerite or pyrite.

Since it has not been shown to have formed by replacement it is desirable to ascertain some likely cause for its precipitation. It is thought that hydrogen sulphide may have been the precipitating agent. Several methods of forming hydrogen sulphide under the existing conditions may be possible (see Prof. Paper No. 80) but omitting a discussion of all but one, it may be said that to the

writer the most probable is that suggested by Allen and Crenshaw.[1]

These investigators find that, so far as determined, wurtzite is always deposited from an acid solution. In the oxidation of the sulphides, including pyrite, free sulphuric acid is formed. This will react with sphalerite to form zinc sulphate and hydrogen sulphide. These together with free acid are present in the solutions that pass into the sulphide zone. By reaction with the minerals the free oxygen is used up and the acidity reduced. Under these conditions the hydrogen sulphide in the solutions will precipitate part of the zinc from the sulphate solution as wurtzite. That the precipitation proceeds much more slowly than that of the copper sulphides is indicated by the much greater vertical extent of the zone of enriched zinc sulphide.

In some of the zinc ores galena has been deposited in the grains of zinc sulphide (both sphalerite and wurtzite) and it is practically certain that there has been a replacement of the zinc sulphide rather than a simple filling of fissures. It is not believed that this alteration has resulted in any important concentration of lead but it may have been an important factor in the alteration of the zinc sulphides—that is, the zinc sulphate may have been formed in part by the reaction of zinc sulphide with lead sulphate rather than by simple oxidation, the action of sulphuric acid, or copper sulphate.

No favorable opportunity was observed for the study of secondary silver sulphides and as already stated it is not believed that they were important, though they were probably formed to a limited extent.

CHANGE IN METALLIC CONTENT.

As already indicated in the discussion of the mineralogical changes that have taken place in the alteration of the ores, there has been a change in the metallic content which has been an important factor in determining the commercial value of the deposit.

[1] Allen, E. T., and Crenshaw, J. L., "The Sulphides of Zinc, Cadmium, and Mercury; their Crystalline Form and Genetic Condition," *Am. Jour. Sci.*, 4th ser., Vol. 34, pp. 341–376, 1912. The reader is referred to this important paper for a discussion of the synthetic formation of the zinc sulphides.

For a number of years the Horn Silver Mining Co. kept a record of the ore mined and the metal content by levels. This is shown in the following tables, the first giving the total ore and the metal content, and the second the content expressed as percentages and ounces per ton.

PARTIAL RECORD BY LEVELS OF THE ORE TAKEN FROM THE HORN SILVER MINE.

	Total Ore, Tons.	Lead, Tons.	Silver, Ounces.	Gold, Ounces.	Copper, Pounds
Cave	2,888.338	1,339.294	69,151.28	14.877	.....
First level	15,263.751	5,644.161	982,943.71	.....	.....
Second level	47,667.035	18,173.67	1,730,093.09	.....	.....
Third level	31,725.30	12,794.469	1,062,755.91	.....	.....
Fourth level	5,351.818	2,325.78	108,129.87	.....	.....
Fifth level	4,140.49	1,363.89	181,717.43	.....	.....
Sixth level	69,667.526	26,221.84	1,823,067.08	178.752	248,682.00
Seventh level	26,796.815	8,564.314	831,493.05	306.713	1,540,885.98
Eighth level	53,620.409	18,327.163	1,535,203.26	522.051	858,433.28
Ninth level	10,959.108	3,095.835	250,823.24	353.238	1,464,248.62
	268,080.59	98,150.415	8,575,377.92	1,375.631	4,112,249.88

PARTIAL RECORD BY LEVELS OF PERCENTAGE OF LEAD AND COPPER AND OUNCES PER TON OF SILVER AND GOLD TAKEN FROM HORN SILVER MINE.

	Lead, Per Cent.	Silver, Ounces Per Ton.	Gold, Ounce Per Ton.	Copper, Per Cent.
Cave	46.37	23.94	0.00515	.....
First level	36.97	64.39	.....	.....
Second level	38.12	36.29	.....	.....
Third level	40.32	33.49	.....	.....
Fourth level	43.45	20.20	.....	.....
Fifth level	32.94	43.88	.....	.....
Sixth level	37.63	26.16	.002565	.1789
Seventh level	31.91	31.02	.01144	2.875
Eighth level	34.18	28.63	.00973	.80
Ninth level	28.24	22.88	.03223	6.68
	36.61	31.98	.005131	.7669

These tables have been compiled from the reports of the Horn Silver Mining Co. without change. Unfortunately they do not represent exactly the levels from which the ore was extracted, but in some instances apparently the level from which it was hoisted. For example, the copper ore that is shown in the tables as coming from the ninth level is stated in another part of the company's report to have come from the seventh and eighth levels.

The following table also shows the metal content of several lots of ore of the different characters represented in the mine:

METAL CONTENT OF SOME ORES FROM THE HORN SILVER MINE.

	1	2	3	4	5	6	7
Gold.....ounces per ton..	.....	.....	1	0.013	0.000	0.000	0.013
Silver.....do....	78.33	51.00	1	6.50	5.59	2.83	10
Lead.....per cent..	50.90	43.50	8	10	9.41	17.41	11.6
Zinc.....do....	0.00	0.00	40	35	35.40	1	20.7
Iron.....do....	3.36	2	4	3	1	1	5.3
Silica.....do....	15.7	2	20	35	1	1	35.4
Sulphur.....do....	.....	2	28	15	1	1	18.0
Copper.....do....	.....	.....	.....	.....	.....	23.7	.....

1. Oxidized ores. Analyses from Hooker report. (See p. 147.)

2. Average of all ores to 300-foot level as determined by Hooker. (See p. 147.)

3. Average yield of 500 tons of zinc ore from seventh level. Emmons, S. F., *Trans. Am. Inst. Min. Eng.*, Vol. 31, 1902, p. 658.

4. Approximate average of zinc ore from 700-foot level, furnished to the writer by general manager M. C. Morris. The sulphur is evidently too low, as it is not sufficient to combine with the metals to form sulphides, though the analysis sums practically to 100 and other general analyses and the study of the ores show that the metals are present as the sulphides.

5. Average of zinc ore shipped in 1905, from company's report.

6. Average of copper ore shipped in 1904, from company's report.

7. Average of shipment of zinc-lead ore from 900-foot level; figures furnished to the writer by general manager M. C. Morris.

So far as the statistics included in these tables are concerned, the oxidized zone may be considered as including the first five levels. The average metal content of ores from these levels, for which there is a record, is lead, 38.99 per cent., and silver, 38.63 ounces per ton. The average in lead and silver of ores hoisted from the ninth level (largely primary) was silver, 22.88 ounces per ton, and lead, 28.24 per cent., while the average of certain shipments as shown in Analysis No. 7, representing the primary zinc lead ore from the 900-foot level, shows silver, 10 ounces per ton, lead, 11.6 per cent., zinc, 20 per cent.

The average of all ores mined has been lead, 33.61 per cent.,

[1] Not reported.
[2] Not estimated.

and silver, 32.04 ounces per ton. It is evident from these figures that the ores in all parts of the main ore body show a definite relation between lead and silver content of approximately an ounce of silver to a unit of lead.

If an ore similar in composition to those of the lower levels, which are regarded as essentially primary, for example Analysis No. 7, should have all the zinc sulphide and a part of the iron removed and the silica content reduced as low as that of Analysis No. 1, representing oxidized ore, the resulting product would be comparable to the average of the oxidized ore. It is evident, therefore, that the lead and silver content of ore in the oxidized zone has been materially increased by the process of alteration, while zinc and copper have been largely removed.

In the relatively small silver ore bodies there has been a marked increase in silver content due to the removal of iron sulphide.

In the zone of sulphide enrichment the zinc content of much of the ore has been raised from probably 20 to 25 per cent. zinc to 35 per cent. or more. This increase has been due to an actual addition of zinc sulphide and possibly to a lesser extent to the removal of other constituents.

As the primary ore carries but a small percentage of copper, it is evident that there has been a marked addition of this metal in the copper ores of the enriched sulphide zone.

In the rich zinc ores there has been a relative decrease in lead due to the addition of zinc, so that these ores contain a lower percentage of lead than either those of the primary zone or the oxidized zone.

Commercially the process of alteration has resulted in the enrichment of the oxidized zone in silver and lead. Primary ores only moderately rich in these metals have been changed to high grade ores. In the zone of sulphide enrichment primary ores that were too low in zinc to be profitably handled, under the existing condtions, have been made of commercial grade, and primary ores that contained very little copper have been converted into rich ores.

THE OXIDATION, SOLUTION, AND PRECIPITATION OF COPPER IN ELECTROLYTIC SOLUTIONS AND THE DISPERSION AND PRECIPITATION OF COPPER SULPHIDES FROM COLLOIDAL SUSPENSIONS, WITH A GEOLOGICAL DISCUSSION.

C. F. Tolman, Jr., and John D. Clark.[1]

In this paper we summarize some of the results of a chemical investigation of the behavior of copper sulphides in electrolytic and colloidal solutions.

We discuss here those phases of the work that appear to the senior author to have a bearing upon the science of ore deposits. Only a portion of the experiments are described, and the descriptions are made as brief as possible. We refer those who desire full details to the bulletin mentioned in the footnote, and in order to facilitate reference to the latter, we shall refer to the experiments according to the numbers used there.

The work was started with the idea of investigating oxidation, solution, and precipitation of copper minerals in acid and neutral electrolytic solutions, such as heretofore have been assumed to be the agents by which downward sulphide enrichment has been accomplished. However, in the course of the study it was discovered that transportation of colloidal sulphides in a dispersed state is accomplished easily by the agency of hydrogen sulphide, that this dispersion is assisted by certain substances, and that almost instant precipitation is brought about by other

[1] These experiments were carried out by Mr. Clark in the chemical laboratories of Leland Stanford Jr. University, and are described in detail in a thesis presented as partial fulfillment of the requirements for the degree of Doctor of Philosophy. This has been published in full as Vol. I., No. 2, Chemical Series, Bulletin University of New Mexico. Grateful acknowledgment is due to Professor S. W. Young, of the Department of Chemistry, Leland Stanford Jr. University, under whose guidance the investigations were carried out.

DESCRIPTION OF PLATE XIV.

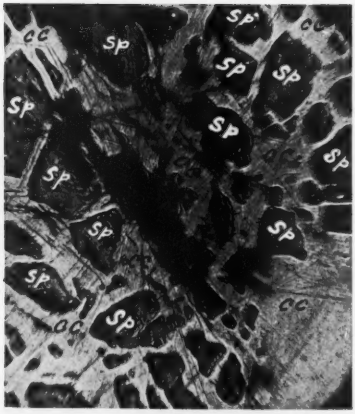
FIG. A. Artificial chalcocite produced as described in experiment 41. Magnified 200 diameters.

FIG. *B*. Chalcocite from Miami, Arizona, from the top of the enriched zone where the solutions were almost certainly acid. Chalcocite (*cc*) replacing sphalerite (*sp*). Magnified 88 diameters.

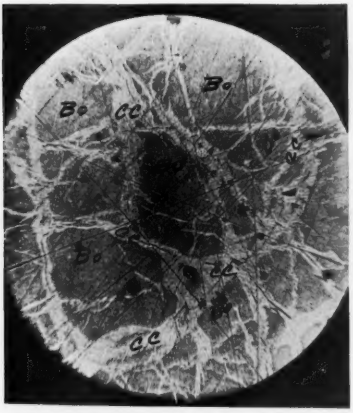
FIG. *C*. Ore from Collahuasi, Chile, collected by B. Bryan and C. L. Severy. Bornite (*Bo*) replaced by chalcocite (acid solutions probably). Magnified 58 diameters.

FIG. *D*. Ore from Engels mine, Plumas County, California. Magmatic chalcopyrite (Cp_1) and bornite (*Bo*) breaking down into covellite and secondary chalcopyrite (Cp_2) and chalcocite. See Turner and Rogers, *loc. cit.* Rock minerals designated *Si*. Magnified 280 diameters.

A


CC
Sp
Sp
Sp
Sp
Sp
Sp
Sp
Sp
Sp
Sp
Sp
Sp
CC
CC

B


Bo
Bo
CC
Bo
Bo
CC

C

COV
Bo
COV
COV
CC
COV
COV
COV
COV
COV
COV
COV
COV

D

substances. As was expected, this dispersion is greatest in alkaline solutions, but to our surprise, it was shown that even in acid solutions dispersion may be sufficient to be of geological importance. Upon removal of the volatile dispersing agents, not only precipitation, but even crystallization of the sulphides was obtained. (See plate XIV., fig. A.)

The application of these results to the explanation of the migration and deposition of ores in both ascending and descending solutions is so patent, and so many explanations were verified that had been half guessed at from geological evidence, and so many lines of new experimental research were suggested, that we believe a report of progress will be of interest to students of ore deposits.

Probably most ore solutions are combinations of colloidal suspensions and electrolytic solutions. These have fundamentally different properties, which must be understood, if one is to follow the complex processes of ore formation. An electrolytic solution may be considered as a suspension of simple (small) molecules and ions in some solvent showing no tendency towards segregation and precipitation on standing. Material thus suspended can be removed from solution only by increasing the number of molecules of any compound in solution beyond its "solubility constant." In addition to the property of continued suspension, the dissolved substances diffuse or spread out until the molecules and ions of each substance are distributed evenly throughout the solvent. On account of the small size of the molecules they can pass through filters, pores of rocks, and fine membranes.

Colloidal solutions[1] consist of suspensions of molecules or discrete particles, showing all variations in size from fairly simple molecules up to masses[2] many thousand times as large as the molecules of electrolytic solutions. These particles are often held in suspension by some dispersive agency, such as hydrogen sulphide or certain potassium salts, which prevent their coagu-

[1] The best books on colloids are: Zsigmondy, "Colloids and the Ultra Microscope," John Wiley & Sons (1909). L. Caserto, "Der Colloide Zustand der Materie," Pisa.

[2] Colloidal silica is composed of very large molecules, the molecular weight of which is estimated at 30,000.

lation, or grouping together in large masses and settling. On the other hand they are rapidly precipitated either by loss of the dispersing agent, or by coagulating agents, such as calcium salts or aluminum oxide. The precipitate may crystallize promptly or settle out as a jelly, through which the electrolytes in solution may diffuse, and upon which they may react, removing certain substances, segregating others, or adding new material. While the colloidal suspensions of large particles may not be able to pass through the pores of rocks, the finer suspensions have almost the penetrating power of electrolytic solutions.[1] For example, the infantile paralysis bacteria pass through a Berkefeld porcelain filter. However, dispersions do not diffuse strongly, like electrolytic solutions, and for this reason we believe are transported only by moving solutions and not by diffusion. For the same reason the amount suspended may vary in different portions of the solvent, and the suspended matter may be more or less heterogeneous in composition.

A. EXPERIMENTS ON THE OXIDATION, SOLUTION, AND PRECIPITATION OF COPPER IN ELECTROLYTIC SOLUTIONS.

I. On the Oxidation of Copper and Iron Sulphides.

In a series of experiments, mixtures of sulphide minerals of copper and iron were treated by percolation with various oxidizing agents, even such active substances as pure oxygen, hydrogen dioxide and manganese dioxide were used. These experiments were successful in oxidizing the pyrite of the mixture, but the copper was held back by the protective action of the unoxidized sulphides. When the tubes were placed in a horizontal position, with openings at both ends to admit a current of air, and were partly filled with the sulphides and the solutions, and slowly revolved so as to cause an alternate wetting and drying, a rapid solution of both iron and copper took place. These experiments confirm the conclusions of Spencer[2] in regard to the importance of alternate wetting and drying in the zone of oxidation.

[1] Zsigmondy, *opus cit.*, Plates III. and IV.

[2] "Chalcocite Enrichment," ECON. GEOL., Vol. VIII., pp. 630-632.

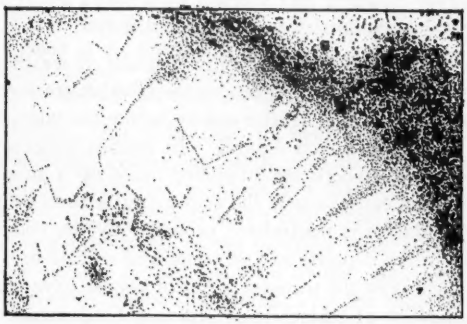


FIG. 130. Thin section of ore from Clarmont ore shoot, Goldfield, Nevada, showing the bands and zones of impurities segregated by the crystallization of the quartz. The bands include specks of free gold. Ore from 1,200 ft level. Magnification = 160 diameters — nicol out.

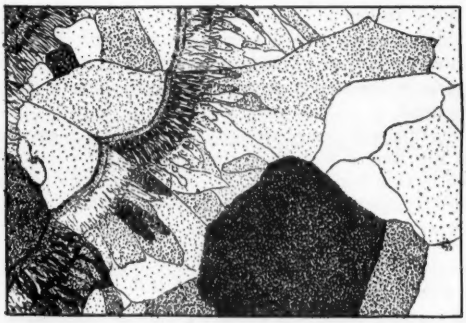


FIG. 131. Thin section of ore from Creede, Colorado. The gangue is quartz with a band of chalcedonic material. Magnification 60 diameters — nicols crossed.

II. *On the Solution of Oxidized Copper Minerals, Especially Copper Silicates and Copper Carbonates by Water Saturated with Carbon Dioxide.*

Studies[1] of copper deposits within the belt of weathering suggest that the copper may migrate as the bicarbonate, or that such minerals as chrysocolla, azurite and malachite are taken into solution by means of carbon dioxide. In certain disseminated deposits, especially where the sulphides make up a small portion of the ore, and consequently the acid manufactured by the processes of oxidation is neutralized promptly by the country rock, as well as in the deposits of carbonate and silicate ores in limestone, evidences of the transportation of copper have been noted.

The solubility of malachite at ordinary temperature in water containing carbon dioxide is stated to be 1 in 3,330, but as copper[2] silicate and carbonate minerals may be transported colloidally, the following preliminary experiments were undertaken:

Experiment No. 7[3].—12 gas washing bottles were taken. To each of 3 was added 30 c.c. *N/2* potassium carbonate; to each of 3 others 30 c.c. potassium carbonate, with a little sodium silicate; to each of 3 others 33 c.c. of dilute sodium silicate solution; and to each of 3 others 30 c.c. of water, thus making 3 sets of 4 liquids in each set. 1 gram 200-mesh malachite was added to each bottle in one set, 1 gram 200-mesh azurite to each bottle in the second set, and 1 gram 200-mesh chrysocolla to each in the third.

Carbon dioxide was passed through each bottle for one month. At the end of this time it was found that there was a trace of copper in the solution in each bottle, the liquids coming from the bottles containing chrysocolla and water, azurite and *N/2* potassium carbonate, and azurite and water giving the strongest tests.

Experiment No. 8.—Amount of copper going into solution or suspension from azurite and from chrysocolla.

To a gas washing bottle was added 1 gram 200-mesh chrysocolla and 100 c.c. water, to a second 1 gram 200-mesh azurite and 100 c.c. water,

[1] Tolman, C. F., "Secondary Sulphide Enrichment of Ores," *Min. and Sci. Press*, Vol. 106, p. 40 (1913), and separate, p. 16.

[2] Liesegang, "Geologische Diffusionen," p. 53.

[3] All experiments were carried on in the light and at ordinary laboratory temperatures, except where otherwise stated.

and to a third 1 gram 200-mesh azurite and 100 c.c. $N/2$ potassium carbonate.

Carbon dioxide was passed through each bottle very slowly for 96 days. The liquid in the first bottle was filtered and analyzed. It contained 0.0004 g. copper. The liquid in the second contained 0.0007 g. copper, and the liquid in the third 0.0007 g.

We conclude, therefore, that in neutral or alkaline solutions, the minerals azurite, malachite, and chrysocolla are easily transported by carbonated solutions, but that without excess of carbon dioxide such action does not take place. The remaining important minerals found in the oxidized zone, such as native copper, the various copper and iron oxides, etc., probably are not transported in appreciable amounts by the action of carbon dioxide. We believe that these observations have a bearing on the question discussed by Bard, and Welsh and Stewart[1] as to the effect of calcite gangue on downward enrichment.

B. THE PRECIPITATION OF COPPER SULPHIDE FROM ACID AND NEUTRAL ELECTROLYTIC SOLUTIONS.

Geological evidence suggests that copper sulphide is precipitated from downward moving acid solutions, although exaggerated[2] notions as to the acidity of these solutions have resulted from analyses of water from mine workings where oxidation and manufacture of sulphuric acid is artificially accelerated. Experimentally some difficulty has been encountered, especially by Grout,[3] in forming chalcocite by the action of acidulated copper-bearing sulphate solutions upon various sulphides.

The formation of a copper-bearing sulphide from acid electrolytic solutions may take place in the following ways:

1. By the substitution of a copper radical for that of a sulphide of lower solution tension.

2. Precipitation by amorphous sulphur.

[1] ECON. GEOL., Vol. 5, pp. 59–61 (1910); Vol. VII., pp. 785–788 (1912).

[2] Emmons and Harrington, "A Comparison of Waters of Mines and of Hot Springs," ECON. GEOL., Vol. VIII., pp. 653–670.

[3] "On the Behavior of Cold Acid Solutions of Copper, Silver, and Gold with Alkaline Extracts of Metallic Sulphides," ECON. GEOL., Vol. VIII., pp. 407–433 (1913).

3. By the reaction of a thiosulphate solution upon copper sulphate.

4. Precipitation by hydrogen sulphide.

III. The Formation of Chalcocite in Acid Solutions.

Little success was obtained in forming a precipitate by the direct action of acid copper sulphate solutions upon pyrite, except in the presence of sulphur dioxide. The experiment carried out by Tolman and described by Winchell,[1] was repeated, and the importance of the impurities in the pyrite, in assisting in the formation of chalcocite was noted.

It was established that sulphur dioxide plays the rôle of a strong reducing agent, as through its use, a crystalline cuprocupric sulphite was produced (Experiment No. 10). In all solutions in which this gas was used, the precipitation of copper sulphide was greatly increased (Experiment No. 20). It is interesting to note in this connection, that chalcocite is not as readily precipitated in the presence of ferrous sulphate as in its absence, although the latter has been thought to be an almost indispensible agent for the securing of chalcocite precipitation. However, the introduction of sulphur dioxide into solutions containing ferrous sulphate, greatly increased this deposition (Experiment No. 20).

Experiment No. 9.—Synthesis of chalcocite.

The experiment as described by Winchell was repeated. A lump of exceedingly pure pyrite was taken and placed in a solution of copper sulphate (1 c.c. = 0.019665 g. Cu) whose acidity with sulphuric acid was *N*/20. This was then saturated with SO_2 and the whole was sealed in a bottle.

At the end of 18 days a faint trace of dark material appeared on some of the surfaces of the pyrite. At the end of one month, one end of the pyrite was strongly coated while the other was as bright as ever. At the end of five months a uniform black coating covered the pyrite.

Experiment No. 10.—Attempted synthesis of chalcocite (Winchell-Tolman experiment modified).

Because the tarnishing of the pyrite was so long delayed in experiment No. 9, it was believed that impurities were necessary for the

[1] Winchell, H. V., "Synthesis of Chalcocite and Its Genesis at Butte, Montana," *Bull. Geol. Soc. Amer.*, Vol. XIV., pp. 272–275 (1901).

formation of chalcocite, and as the analysis of the pyrite used by Winchell and Tolman showed the presence of zinc, a crystal of sphalerite was wired to a piece of very pure pyrite such as was used in No. 9 and the flask was sealed.

At the end of 46 days no marked change could be seen. On the 47th day the flask was accidentally subjected to great jarring and on the 48th day small ruby red crystals were seen. These were prismatic, had high relief, were pleochroic and had parallel extinction. They gave all the tests for cupro-cupric sulphite as described by Segerbloom in his "Table of Properties."

This experiment confirms the belief of Winchell and Spencer that SO_2 plays the rôle of a strong reducing agent. It also tends to confirm the opinion of Lindgren that pyrite does not precipitate Cu_2S or CuS, while zinc blende is present. Neither sulphide formed after months of standing.

IV. *Amorphous Sulphur as a Precipitant of the Copper Sulphides.*

In a number of experiments, and under a variety of conditions, amorphous sulphur was found to precipitate a sulphide of copper from copper sulphate solution, this action being rapid with fresh amorphous sulphur, prepared by the action of hydrogen sulphide on sulphur dioxide freed from the gases and suspended in water, yet falling off rapidly as the sulphur aged. Experiment No. 19 shows this action. (See Fig. 132.) That sulphur should react in this manner is not at all surprising. The equation, $3S + 2H_2O = 2H_2S + SO_2$, is known to be reversible. The work of Stokes[1] readily accounts for the presence of amorphous sulphur in the zone of precipitation.

Several instances of the production of amorphous copper sulphides by the action of sulphide minerals, particularly pyrite, on copper sulphate solution are shown in experiments No. 20, No. 21, and No. 35.

Experiment No. 19.—The effect of age on the precipitating power of amorphous sulphur.

Early in this work it was noticed that freshly prepared amorphous sulphur precipitated copper sulphide from solutions of copper sulphate much more readily than the older materials.

[1] ECON. GEOL., 2, 14–23, 1907.

In order to bring out this fact somewhat quantitatively, H_2S and SO_2 were brought together to produce amorphous sulphur. This when free from the gases was put into suspension with water, and more than enough of this sulphur to precipitate a given amount of copper from a sulphate solution was added to each of seven bottles, the same amount being added to each bottle. A given amount of copper sulphate solution was added to one bottle at once, to a second at the end of 24 hours, to a third at the end of 48 hours, etc. Each bottle was then shaken and allowed to stand for 24 hours when its contents were filtered and analyzed.

The results of the experiment are shown in the accompanying curve. (See Fig. 132.)

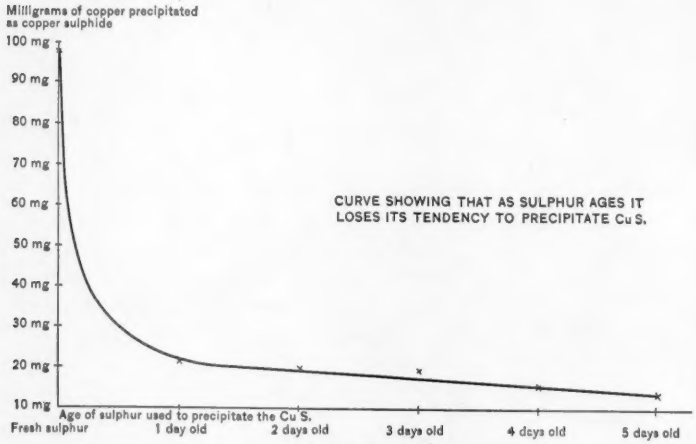


FIG. 132.

V. *The Action of Thiosulphate Solutions on Copper Sulphate.*

Amorphous copper sulphides were produced by the action of a thiosulphate solution on one of copper sulphate. This action at first formed the double thiosulphate of sodium and copper, which then decomposed to give a mixture of amorphous cupric and cuprous sulphides. Details of this work, and references showing this action to be possible geologically, are given in experiments Nos. 18 and No. 24.

Experiment No. 18.—Production of Cu_2S by the use of $Na_2S_2O_3$.

The rapid precipitation of Cu by amorphous S suggested the attempt to get this S from the decomposition of a thiosulphate, as Hillebrand[1] seems to have found thiosulphates in deep mine waters, and as Stokes[2] had shown that thiosulphates are produced when alkaline solutions act on pyrite.

Three flasks were taken and to each was added 50 c.c. CuSO solution (1 c.c. = 0.039331 g. Cu). To the first was added 5 c.c. *N/2* $Na_2S_2O_3$; to the second 25 c.c., and to third 50 c.c. of this thiosulphate solution. Each flask was given an atmosphere of CO_2 and was sealed.

In each flask the double thiosulphate of sodium and copper formed at once and then began to decompose. The contents of the first flask were black in two days, in the second flask in five days, and in the third at the end of several weeks.

The formation and decomposition of the double thiosulphate of sodium and copper, which according to Dutoit[3] has the copper in the cuprous condition, goes in several steps or stages. When the two solutions are mixed tiny yellow prisms are formed. These on standing produce long yellow needles, which begin to splinter, even going so far as to be a mass of radiating splinters, and these splinters decompose to a black sulphide, decomposition first taking place at the end of the splinters.

At the end of 71 days the residue in the second flask was washed with water and with alcohol, and was extracted with CS_2 and analyzed. 0.5035 g. of the residue gave 0.1563 g. S thus leaving 0.3472 g. Cu.

0.5035 g. Cu_2S contains 0.4022 g. Cu and this amount of CuS contains 0.3347 g. On the basis of the copper content this residue was 21.74 per cent. Cu_2S.

Experiment No. 24.—Cu_2S from the double thiosulphate of sodium and copper.

Some of the double thiosulphate was prepared from solutions of copper sulphate and sodium thiosulphate. This was washed and sealed in a flask with an excess of water and an atmosphere of CO_2.

After 8 weeks the material in the flask began to gather into large platy masses which stood up on one edge in the solution. This continued until the material in the flask was well compacted into large platy masses.

The flask was opened at the end of 123 days, and the residue was washed with water and alcohol, was dried and extracted with CS_2 and analyzed.

[1] 17th Ann. Rep. U. S. G. S., Part 2, p. 21, 1896.

[2] H. N. Stokes, "Experiments on the Action of Various Solutions on Pyrite and Marcasite," ECON. GEOL., 2, pp. 14–23, 1907.

[3] Pierre Dutoit, "Sur les hyposulphates cupro alkalins," *Jour. Chemie Physique*, 2, 4, pp. 650–673, 1913.

0.5170 g. of the residue gave 0.1380 g. S thus leaving 0.3790 g. Cu. 0.5170 g. of Cu_2S contains 0.4130 g. Cu, while this weight of CuS contains 0.3437 g. Cu. On the basis of the copper content of this residue it contained 50.94 per cent. Cu_2S.

VI. *The Formation of Hydrogen Sulphide.*

Difference of opinion appears in geological literature[1] as to the importance of hydrogen sulphide in producing chalcocite from acid solutions. Grout found that only pyrrhotite, sphalerite, and alabandite produce the gas in appreciable amounts from dilute acid solutions, and in the presence of acid copper sulphate solutions only the last named sulphide is "active." In our experiments hydrogen sulphide was produced by the action of water on pyrite, and it was also produced by the action of very dilute acid on pyrite, chalcopyrite, and bornite, the relative development of hydrogen sulphide decreasing as the iron content of the minerals decreased.

The probability that this gas may be produced in nature's laboratory is suggested in experiments 22 and 23. That the evolution of hydrogen sulphide was not recognized by Grout in acid copper sulphate solutions, is not considered by us to be important geologically. The evolved gas would react on copper sulphate to form copper sulphides, and the latter may remain suspended in so fine a colloidal state as not to be readily recognized (see experiment No. 43 described below), or under the condition of Grout's experiments the solubility product for the copper sulphides may not have been exceeded.

Experiment No. 22.—H_2S produeed by hydrolytic action of water on pyrite.

Several one-half gram portions of uniform sized pyrite particles, ranging from those which passed through the 20-mesh sieve and were retained on the 30-mesh to those which passed through the 200-mesh sieve, were sealed, each portion in a separate tube, with 20 c.c. of water.

These tubes were kept at about 41 degrees for three months, when the tube containing the 80–90-mesh pyrite was opened, its contents filtered and tested colorimetrically with a standard solution of lead nitrate. The test showed the presence of H_2S in solution. Other tubes were afterward tested and their contents gave like results.

[1] Grout, F. L., *loc. cit.*, pp. 423–424.

Experiment No. 23.—Production of H_2S from pyrite, chalcopyrite, and bornite.

Duplicate tubes containing (*a*) 0.5 g. 200-mesh pyrite and 15 c.c. *N*/10 sulphuric acid, (*b*) 0.5 g. 200-mesh chalcopyrite and 15 c.c. *N*/10 sulphuric acid, (*c*) 0.5 g. 200-mesh bornite and 15 c.c. *N*/10 sulphuric acid, were sealed and placed in a thermostat at about 41 degrees for 51 days.

The contents of one set of tubes were filtered and the filtrates treated with standard lead nitrate solution. All showed the presence of H_2S in solution, the pyrite having set free the most and the bornite the least.

The duplicate set was then put in an autoclave and heated at 195 degrees for two hours. The tube containing the acid and pyrite exploded, the one containing the acid and chalcopyrite cracked, and the one containing the acid and bornite remained intact, though much pressure was developed by the H_2S inside. This H_2S was readily noticed because of its odor.

The fact that sulphur dioxide assisted in the formation of chalcocite may be explained by the fact mentioned above, that this acts on hydrogen sulphide as follows:

$$2H_2S + SO_2 = 2H_2O + 3S,$$

and the tendency towards colloidal dispersion of the copper sulphide is decreased, and the precipitation of the same is assisted by the amorphous sulphur. We believe that colloidal sulphur is an important precipitant for copper sulphide in both acid and neutral solutions.

VII. *The Effect of Neutralization on the Precipitation of Copper Sulphides.*

The tendency towards precipitation as the solutions are neutralized, has been pointed out in literature,[1] and seems evident from mere inspection of the chemistry of the process. Sulphur dioxide was found to accelerate the formation of a precipitate under a variety of conditions.

Experiment No. 20.—Precipitating power of pyrite in various solutions.

[1] Sullivan, E. C., "The Interaction between Minerals and Water Solutions, with Special Reference to Geologic Phenomena," Bull. U. S. G. S., 312, pp. 37–66. Grout, *loc. cit.*, pp. 424–426.

With a view of ascertaining those conditions most favorable for the precipitation of Cu as a sulphide from $CuSO_4$ solutions by means of pyrite, and with a view of securing more data on the rôle of SO_2, a given amount of 200-mesh pyrite was sealed in tubes with (1) an aqueous solution of $CuSO_4$, (2) an aqueous solution of $CuSO_4$ saturated with SO_2, (3) a solution of $CuSO_4$ and $FeSO_4$, (4) a solution of $CuSO_4$ and $FeSO_4$ saturated with SO_2 and (5) an acidified solution of $CuSO_4$ (H_2SO_4 used) which was isotonic with aqueous solution which had been saturated with SO_2. These tubes were shaken once daily and at the end of 47 days their contents were analyzed.

The results showed that the amounts of copper precipitated increased with the concentration of the $CuSO_4$ solution, that great precipitation takes place in aqueous solution, and that this is increased by the presence of SO_2. The results also showed that the precipitation in the presence of $FeSO_4$ is not as great as in its absence, but that SO_2 increases this precipitation in $FeSO_4$.

They showed that the reducing action of SO_2 and not the action of the H ion is responsible for the increased precipitation in the presence of this substance. Moreover they showed that neutrality or alkalinity are conditions most favorable for precipitation.

Details are given in the following table:

TABLE II.

	1. Amt. Cu Ppted. from Water Solution of $CuSO_4$.	2. Amt. Cu Ppted. from Water Sol. of $CuSO_4$ Sat. with SO_2.	3. Amt. Cu Ppted. from Approx. N/10 $FeSO_4$ Sol. of $CuSO_4$.	4. Amt. Cu Ppted. from Approx. N/10 $FeSO_4$ Sol. of $CuSO_4$ Sat. with SO_2.	5. Amt. Cu Ppted. from H_2SO_4 Sol. of $CuSO_4$ Isotonic with Sol. in Column 2.
1 g. pyrite 22 c.c. liquid containing 0.0787 g. Cu as $CuSO_4$	0.01325	0.0240	0.0113	.....	Negligible
1 g. pyrite 24 c.c. liquid containing 0.1573 g. Cu as $CuSO_4$	0.0259	0.0446	0.0187	0.0119[1]	Negligible
1 g. pyrite 26 c.c. liquid containing 0.2360 g. Cu as $CuSO_4$	0.0277	0.0677	0.0250	0.0295	Negligible
1 g. pyrite 28 c.c. liquid containing 0.3146 g. Cu as $CuSO_4$	0.0364	0.0972	0.0318	0.0462	Negligible

[1] Probable experimental error.

C. EXPERIMENTS REGARDING THE PHYSICAL AND CHEMICAL BEHAVIOR OF COLLOIDAL PRECIPITATES AND SUSPENSIONS OF COPPER SULPHIDES.

As is well known, freshly precipitated copper sulphide is a colloid. In the experiments summarized here, all copper sulphide precipitates were colloidal at first, with the possible exception of the slow crystalline growth deposited upon pyrite from acid solutions in the presence of SO_2. We summarize our results under the following headings: First, the formation of colloidal amorphous copper sulphides; second, the chemical conduct of amorphous copper sulphides, and third, the physical conduct of amorphous copper sulphides.

VIII. *The Formation of Colloidal Copper Sulphides.*

The formation of copper sulphides from electrolytic sulphate solutions has been considered above. In addition to this it was found that both artificial precipitates and massive copper sulphide minerals may be dispersed, and then precipitated by the removal of the dispersing agents. The dispersion is caused chiefly by the presence of hydrogen sulphide, less rapidly by sulphur, and takes place in acid solutions, neutral solutions, and especially in alkaline solutions. This dispersion and subsequent precipitation is shown well in experiments 40, 41, 43 and 44. As examples of this action we give the following:

Experiment No. 41.—Production of chalcocite crystals, and the effect of H_2S as a dispersing agent.

2 grams of 200-mesh chalcocite were put into a tall Bessler tube and covered with 25 c.c. of a KHS solution. H_2S was passed through the solution for an hour.

The same amount of chalcocite was put into a tube and covered with 25 c.c. of a K_2S solution. Hydrogen was passed through this solution for an hour.

The same amount of chalcocite was put into another tube and was covered with 25 c.c. of a solution of equal parts of K_2S and KOH. Hydrogen was passed through this liquid for an hour.

Each solution contained approximately the same amount of potassium. The gases were passed through the liquids at approximately equal rates.

The material in the first tube showed strong dispersion; that in the

second showed one fourth to one sixth as much; and that in the third showed scarcely any.

At the end of 10 days it was noted that the material in the second tube had risen, and that a small mass having something of a crystalline appearance floated on the surface. From this hung down a growth resembling a fox's tail.

This growth and "tail" was washed, and the latter examined with a microscope. This "tail" was seen to be made up of a lot of stiff black, non-transparent hairs or rods. One or two were especially large and showed truncated ends. The angles on the ends of one rod were measured. Beginning on the right side of the rod or prism and going anti-clockwise the angles were approximately 37, 51, and 56 degrees (see Plate XIV., Fig A).

The floating mass was washed again with water and with absolute alcohol and then dried. It was found to weigh 13 mg. It was analyzed with the greatest care and was found to yield 2.57 mg. S and 10.40 mg. Cu. 13 mg. of Cu_2S would yield 10.39 mg. Cu. The floating mass was certainly cuprous sulphide. We assume that the crystals were of the same composition.

Experiment No. 43.—The dispersing power of H_2S in acid solution.

To determine the dispersing power (relative) in acid solution four gas washing bottles were taken. To the first, 2 grams of 200-mesh chalcocite was added. To the second, 2 grams of 200-mesh covellite; to the third, bornite; and to the fourth, chalopyrite. 50 c.c. of $N/10$ sulphuric acid was added to each bottle. H_2S was passed through the four bottles for a few minutes each day for four weeks.

At the end of this time all the minerals were slightly dispersed, this dispersion appearing most in the chalcocite and least in the chalcopyrite.

The contents of the bottles were filtered. All of the filtrates appeared clear, though that from the chalcocite gave the merest suggestion of being less clear than the others.

Lumps of zinc were added to each filtrate. In the chalcocite filtrate a brownish black cloud appeared at once around the zinc. This cloud did not appear in the others though they became less clear.

The residues which were left in the tubes containing the filtrates after the zinc had gone into solution were dissolved in nitric acid, and this acid was more than neutralized with NH_4OH. All showed traces of copper the test being strongest in the residue from the chalcocite filtrate, and least in that from the chalcopyrite. A very noticeable amount of $Fe(OH)_3$ was observed in the tube containing the residue from the bornite filtrate.

This experiment showed clearly that H_2S disperses these minerals in acid solution and that the dispersion is in a measure proportional to

their copper content. It also shows that in acid solution and in contact with H_2S bornite gives up some of its iron.

Dispersion in acid solution is very much less than in alkaline. The dispersed material is so finely divided that it passes with ease through a filter.

IX. *The Chemical Behavior of the Copper Sulphates.*

Linder and Pictou[1] believe that dispersed sulphides are in unstable combination with hydrogen sulphide, because their analyses of the dispersed material show an excess of sulphur over that contained in the precipitated sulphides.

X. *Spontaneous Decomposition of Cupric Sulphide into Cuprous Sulphide and Sulphur.*

An important discovery of the investigation is that at ordinary temperatures, cupric sulphide in contact with water spontaneously decomposes into cuprous sulphide and sulphur.

$$2CuS = Cu_2S + S.$$

This decomposition was determined in experiments 12, 15, 17, 18, 24, 26, 27, 29, 30, 31, and 34. Experiment 31 is an example of this action

Experiment No. 31.—Production of Cu_2S. (This is the experiment in which the spontaneous change of CuS to Cu_2S and S was first noted.)

A solution of $CuSO_4$ had H_2S passed through it until all the copper was precipitated as the sulphide. The precipitates were freed from solution by filtration, and then this precipitate was placed in a flask with a lump of chalcocite weighing 2.2861 g. and the whole covered with water and sealed in an atmosphere of CO_2.

After 54 days the flask was opened. The lump weighed 2.1404 g.—a loss of 0.1457 g. The residue under the microscope was seen to be made up of particles of black sulphide which were intermingled with particles of sulphur. The residue was extracted with CS_2 (which was known to be free from dissolved S) and the extract evaporated. A yellow residue, which by the microscope and by chemical test was shown to be sulphur, was left upon evaporation of the CS_2.

[1] "Some Physical Properties of Arsenious Sulphides and Other Solutions," *Jour. Chem. Soc.*, Vol. 67, p. 63 (1895).

The residue from which the sulphur had been extracted was analyzed for both S and Cu, and upon the basis of its Cu content was shown to be 43.64 per cent. Cu_2S. Thus the transformation of CuS to Cu_2S was shown.

In general it was found that the transformation was retarded by an excess of sulphur, and strange to say does not take place as readily in presence of ferrous sulphate as in its absence. Fraulein Wassjuchnowa[1] has shown that this decomposition takes place in the dry state at temperatures above 500° C.

XI. *Sulphides Precipitated in Acid Conditions Compared with Those Formed in Alkaline Solutions.*

From the chemistry of the subject, we believe that the copper sulphides formed in an acid environment should be of a different mineralogical composition than sulphides formed in alkaline solutions. A well known analytical method for the separation of copper from iron is based on the fact that hydrogen sulphide precipitates the former, and not the latter, in acid solutions. While this does not prove that iron and iron-copper sulphide minerals cannot form in acid solutions, we believe that the tendency will be decreased, while in alkaline solutions, iron and copper sulphides and complex sulphosalts form readily. Later the iron may be eliminated by an attack of acid solutions, or even in alkaline solutions, by an electrolytic diffusion of iron out of the colloidal precipitate. Geological applications along these lines will be mentioned later.

D. THE PHYSICAL BEHAVIOR OF COLLOIDAL COPPER SULPHIDES.

XII. *Relative Dispersion of Chalcopyrite, Bornite, Covellite, and Chalcocite.*

Experiments on the degree of dispersion of the copper bearing sulphide minerals show that (1) chalcopyrite is least dispersed and the rest follow in this order: (2) bornite, (3) covellite, and (4) chalcocite.

Experiment No. 39.—Solution and deposition of chalcocite.

Some 200-mesh chalcocite was put into a strong solution of KOH,

[1] *Zeits. f. Electrochemie*, Vol. 19, p. 902 (1913).

and H_2S was passed through the solution, which was kept cold, until the solution was saturated. The heavy dense chalcocite became colloidal, occupying 4 or 5 times its original volume. This whole solution was heated in an autoclave at 180 degrees for one and a half hours. The solution became deep yellow. This was filtered through glass wool, and was then gently heated on an air bath. H_2S came off slowly and finally black lumps gathered on the bottom of the container.

A drop of this filtrate just mentioned was evaporated on a glass slide, and its residue under the microscope showed black needles or prisms together with some yellow prisms suggestive of the double thiosulphate of sodium and copper. Some of this same filtrate was neutralized with dilute sulphuric acid whereupon a brownish black precipitate was formed. This gave a strong test for copper.

Experiment No. 40.—Solution and deposition of a copper sulphide derived from covellite, bornite and chalcopyrite.

Experiment No. 39 was repeated with each of the minerals named above.

The filtrate from covellite behaved as did the filtrate obtained in No. 39. A few of the hairs as observed in experiment No. 39 were noted on the glass wool filter.

The filtrate from the bornite behaved as did that from the covellite. It did not contain as much copper however. A large number of the hairs were obtained from the bornite. These gave a strong test for copper.

The filtrate from the chalcopyrite gave only a faint test for copper.

It appeared that the H_2S had dispersed these minerals in the following descending order: chalcocite, covellite, bornite, and chalcopyrite, and that the alkaline liquid with its H_2S had dissolved copper from these minerals in this same order.

The dispersion and solution of the chalcocite was much more marked than were these phenomena with the other minerals.

XIII. *Tendency for Selective Accretion of Copper Sulphide.*

Experiments showed plainly a tendency for the amorphous copper sulphide to accrete on certain minerals, and to deposit from their dispersed condition when those agents which favor dispersion are removed from the solution. In experiment No. 13 it was found that some sulphide had gathered on chalcopyrite, and in No. 29 a heavy dense growth was noted on bornite. Because of the relatively greater accretion on the bornite it would seem that this mineral may become chalcocite through continued

addition of copper sulphide (see also experiment No. 42). The same may be said of chalcopyrite though in the case of this mineral, the action would be much slower. The fact that it is difficult to find a chalcocite which is free from specks of bornite gives additional weight to this view.

Copper sulphide was caused to accrete on sphalerite (experiment No. 30), and also on chalcocite as cuprous sulphide, the phenomena in this case being caused by the removal of a dispersing agent, hydrogen sulphide.

The effect of the removal of this dispersing agent is well brought out in experiment No. 33. Here both crystalline (apparently) and amorphous sulphides were thrown down as the hydrogen sulphide was released. Moreover with a reduction of alkalinity, such as in nature could be accounted for by descending acidic waters mingling with the alkaline solutions, a precipitate of the amorphous sulphide was produced.

With the complete elimination of hydrogen sulphide, crystalline chalcocite was produced, as is seen in experiment No. 41, and a tendency in this direction was noted in experiments No. 38 and 40.

Experiment No. 33.—Growth of Cu_2S on chalcocite.

With a view of getting some experimental verification of the formation of chalcocite as suggested by Prof. A. F. Rogers[1] a lump of chalcocite weighing 4.5240 g. was put into a flask containing CuS and a solution of K_2S which had been completely saturated with H_2S. Testing showed that this liquid held considerable Cu in suspension or solution. A stopper with a Bunsen valve was inserted, thus giving the H_2S which held the copper in suspension, a chance to escape.

At the end of three weeks crystal faces were seen shining on the chalcocite lump.

At the end of 85 days the flask was opened and the solution displaced by water. The chalcocite lump was washed with hot water until it was free from alkali. One could see that the lump was coated and that this coating had on it tiny shining spots suggestive of crystal faces. The lump was dried. It weighed 4.5874 g.—a gain of 0.634 g. 32.24 milligrams of this coating was taken for analysis. This gave 8.403 mg. of S, thus leaving 23.837 mg. of Cu. 32.24 mg. of pure chalcocite would give 25.748 mg. Cu.

This sulphur figure was a little too high. As no extraction of CS_2

[1] A. F. Rogers, ECON. GEOL., 8, p. 781, 1913.

was made it is quite possible that a small amount of S may have been in the material deposited on the chalcocite.

We conclude that a relatively pure chalcocite was produced from this alkaline solution.

The analysis of the residue in the flask showed that it had a Cu_2S content of 57.63 per cent.

XIV. *The Effect of Sulphur on the Dispersion of Copper Sulphide.*

Free amorphous sulphur has the effect of dispersing a massive or crystalline sulphide. This is forcefully shown in experiment No. 13. In about four months a lump of chalcocite weighing seven grams lost over one gram in weight when sealed in a flask in contact with this amorphous sulphur.

Experiment No. 13.—To observe transference, substitution, or growth. A lump of chalcocite weighing 7.6332 g. and a lump of chalcopyrite weighing 3.2458 g. were sealed in a flask with 50 c.c. copper sulphate solution (1 c.c. = 0.039331 g. Cu), 50 c.c. ferrous sulphate solution (1 c.c. = 0.02624 g. Fe), and a large excess of amorphous sulphur (2 days old) and an atmosphere of carbon dioxide.

A decided growth of black material was observed on and in contact with the chalcocite at the end of two weeks. The chalcocite lump remained attached to the bottom of the flask. This lump was covered with a black velvety film which stood out in ridges on the lump. The film (very loosely attached) was removed and the lump weighed. It weighed 6.5745 g.—a loss of 1.0587 g.

This film and the general residue in the flask were analyzed. Both contained iron which made exact results as to Cu_2S and to CuS of little value. The fact that the film had a copper content of 69.03 per cent. Cu, while the general residue contained 64.73 per cent., showed the greater copper content to be nearer the lump of chalcocite.

It seems probable that in the presence of the excess of amorphous sulphur, the sulphide was mostly CuS though some Cu_2S was probably present in the film.

The chalcopyrite lump was loose and came out of the flask readily. It weighed 3.2473 g.—a gain of 0.0015 g. A deposit of black sulphide hung tenaciously to the lump and could not be washed off. This would account for the gain, and would indicate that chalcocite can grow on, or at the expense of chalcopyrite, but not as readily as on or at the expense of bornite. See experiment No. 29.

This experiment was repeated with amorphous sulphur which was one

day old, and similar results were obtained. It was also repeated with freshly prepared amorphous sulphur. The final results were much as given above.

XV. *The Effect of Certain Soluble and Insoluble Substances on the Dispersion of Colloidal Copper Sulphide (a) in the Absence of Hydrogen Sulphide, (b) in the Presence of Hydrogen Sulphide, and (c) in the Presence of Hydrogen Sulphide and Carbon Dioxide.*

One of the peculiar properties of colloids is that their dispersion may be increased greatly, or completely inhibited, by the presence of small amounts of soluble or insoluble foreign matter. Although a satisfactory explanation of such action is not at hand, it is analogous to catalytic action, and is not necessarily accompanied by any chemical reaction.

If, as we believe, dispersion is an important factor in ore genesis, transportation of ores may be assisted by the presence of materials favoring dispersion, and deposition may be localized at those points, and in those rock formations, in which the substances unfavorable to dispersion occur. We have made only a start at investigations along these lines, and the results are to be considered as merely suggestive.

The behavior of sodium and potassium salts were investigated, as we know that ore solutions may contain both but generally the latter. We find that both assist in the dispersion of colloidal copper sulphides, the latter being more effective. The calcium and aluminum salts used in these experiments bring down the dispersed matter, and a still more rapid precipitation is induced by the insoluble dehydrated aluminium oxide. It is unnecessary to call the attention of geologists to the well-known precipitative action of the limestone, clay gouge and aluminous matter.

Experiment No. 45.—Flocculation of colloidal copper sulphide.

Some colloidal copper sulphide was prepared, and was carefully freed from the presence of any electrolyte by washing.

Equal portions of this colloidal material were put into flasks, and were treated with NaCl, KCl, $CaCl_2$, $CaCO_3$, $AlCl_3$ and Al_2O_3, as can be seen in detail in the accompanying table.

It was found that the presence of NaCl or KCl increased the amount of the sulphide which was held in suspension, whereas $CaCl_2$, $CaCO_3$, $AlCl_3$, and Al_2O_3 caused the colloid to flocculate. This flocculation was rapidly accomplished by the Al_2O_3.

A similar set of solutions with the colloidal sulphide were treated with H_2S. The hydrogen sulphide increased the amount of material which was held in suspension by water, NaCl solution, and KCl. It also carried into suspension some copper sulphide which had been flocculated by the $CaCO_3$. The H_2S failed to act on the colloid which had been precipitated by $CaCl_2$, $AlCl_3$, and Al_2O_3.

A similar set of solutions with the colloidal copper sulphide were treated with H_2S and CO_2. The results were much as those produced with the H_2S alone, except that not as much of the colloid which had been precipitated by the $CaCO_3$ was again put into suspension, which could be accounted for by the fact that CO_2 acting on the carbonate undoubtedly produced calcium ions.

TABLE III.

	A. Suspended Colloid.	*B.* Suspended Colloid, Liquid Saturated with H_2S.	*C.* Suspended Colloid, Liquid Saturated with H_2S and CO_2.
1. Colloidal CuS in water.	Remained suspended.	H_2S caused the amount of suspended colloid to increase.	H_2S and CO_2 caused more colloid to be suspended than in *1B*.
2. Colloidal CuS in N/300 NaCl.	More in suspension than in *1A*.	H_2S caused the amount of suspended colloid to increase.	H_2S and CO_2 caused more colloid to be suspended than in *2B*.
3. Colloidal CuS in N/300 KCl.	More in suspension than in *1A*.	H_2S caused the amount of suspended colloid to increase very much.	H_2S and CO_2 caused more colloid to be suspended than in *3B*.
4. Colloidal CuS in N/300 $CaCl_2$.	Colloid soon flocculated.	H_2S failed to cause the flocculated colloid to disperse.	H_2S and CO_2 failed to cause the flocculated colloid to disperse.
5. Colloidal CuS with 1 gram $CaCO_3$.	Colloid soon flocculated.	H_2S dispersed the flocculated colloid to some extent.	H_2S and CO_2 failed to cause the flocculated colloid to disperse as much as in *5B*.
6. Colloidal CuS in N/300 $AlCl_3$.	Colloid soon flocculated.	H_2S failed to cause the flocculated colloid to disperse.	H_2S and CO_2 failed to cause the flocculated colloid to disperse.
7. Colloidal CuS with 1 gram Al_2O_3.	Colloid flocculated at once.	H_2S failed to cause the flocculated colloid to disperse.	H_2S and CO_2 failed to cause the flocculated colloid to disperse.

XVI. *The Behavior of Colloidal Sulphur.*

The proof that cupric sulphide decomposes into cuprous sulphide and sulphur, and the fact that sulphur is an important precipitating agent in acid and neutral solutions, suggested an in-

vestigation of the dispersion of this substance. We found the fact that massive chalcocite does not contain admixed sulphur to be especially puzzling. The sulphur that has been reported often at the top of the zone of sulphide enrichment[1] does not account for that which must be formed by the processes mentioned above.

In the experiments described below, it was found that carbon dioxide disperses sulphur energetically. This gas increases the dispersion of the copper sulphides when hydrogen sulphide is present, but precipitates them when the latter is absent. We venture the surmise that carbon dioxide and hydrogen sulphide together keep both sulphur and the copper sulphides in a dispersed state; that when hydrogen sulphide escapes, is used up in the process of pyritizing the iron minerals of the country rock, or ceases to flow, the carbon dioxide precipitates the sulphides, but carries on the sulphur which may be used up in the further pyritization of the country rock.

Experiment No. 46.—Flocculation of colloidal sulphur.

Solutions of the substances used in experiment No. 45 were added to colloidal sulphur, and then these solutions containing the colloid were treated with H_2S and with H_2S and CO_2 mixture, exactly as the material was treated in experiment No. 45.

The results are here tabulated.

TABLE IV.

	A. Suspended in Water.	*B.* Saturated with H_2S.	*C.* Saturated with H_2S and CO_2.
1. Water.	S remained suspended.	Sulphur flocculated rapidly.	Much S remained suspended though not as much as in 1*A*.
2. N/300 NaCl.	More S suspended than in 1*A*.	Sulphur flocculated slowly.	Much S remained suspended though not as much as in 2*A*.
3. N/300 KCl.	More S suspended than in 1*A*.	Sulphur flocculated slowly.	Much S remained suspended though not as much as in 3*A*.
4. N/300 $CaCl_2$.	S soon flocculated.	S remained flocculated.	Sulphur dispersed to some slight extent.
5. 1 g. $CaCO_3$.	S soon flocculated.	S remained flocculated.	Sulphur dispersed to some slight extent.
6. N/300 $AlCl_3$.	S soon flocculated.	S remained flocculated.	S remained flocculated.
7. 1 g. Al_2O_3.	S soon flocculated.	S remained flocculated.	S remained flocculated.

[1] Lakes, A., "Vulcan and Mammoth Chimmey Mine," *Trans. Amer. Inst. Min. Engs.*, Vol. 26, pp. 440–448 (1896).

Experiment No. 47.—Dispersing and flocculating effects of H_2S, SO_2, and CO_2 on colloidal copper sulphide and on colloidal sulphur in water and in the presence of $N/1400$ $KCl + K_2CO_3$.

A colloidal copper sulphide prepared as described in experiment No. 45. A colloidal sulphur solution was prepared by the action of H_2S on SO_2, the sulphur then being suspended in water. Portions of each colloidal solution were saturated with H_2S, SO_2, and CO_2, and then portions to which K_2CO_3 and KCl had been added so that the K ion was $N/1400$, were saturated with these gases.

The results are here tabulated.

TABLE V.

	Water Suspension of Colloid.	$N/1400$ $KCl + K_2CO_3$ Suspension of Colloid.
H_2S	H_2S caused sulphur to flocculate rapidly.	H_2S caused sulphur to flocculate slowly.
SO_2	SO_2 did not flocculate the S rapidly.	SO_2 did not flocculate the S rapidly.
CO_2	CO_2 practically prevented the flocculation of the S.	CO_2 prevented the flocculation of the S.
H_2S	H_2S kept the copper sulphide dispersed for a long time.	H_2S practically prevented flocculation of the copper sulphide.
SO_2	SO_2 caused the copper sulphide to flocculate.	SO_2 caused the copper sulphide to flocculate.
CO_2	CO_2 caused a very clean cut flocculation of the copper sulphide.	CO_2 caused a very clean cut flocculation of the copper sulphide.

E. GEOLOGICAL APPLICATION.

Certain geological applications of the above have been suggested or are self evident. We venture only a brief summary of the bearing of these ideas on the present-day philosophy of ore deposition, and for the sake of clarity, beg indulgence for the repetition of many of the points already touched upon.

The experiments were undertaken with the idea of investigating enrichment, especially downward enrichment of sulphide ores, and although the conclusions have a much wider application, we start with this subject.

XVII. *Downward Sulphide Enrichment.*

We believe that this is initiated in an acid environment, but the solutions probably change to a neutral and then an alkaline condition.[1]

[1] See Grout and Emmons, *loc. cit.*

The precipitation of sulphides from acid solutions is believed to take place in the presence of pyrrhotite, sphalerite, and pyrite where sulphur dioxide is present. Acidity should be prominent towards the top of the sulphide zone, and theory suggests that chalcocite formed under these conditions should be relatively free from iron, and acidity should not favor the development of the complex mixtures that are formed under alkaline conditions. Inasmuch as neutralization accompanied by increased precipitation probably takes place in an irregular manner in every ore body, and perhaps in certain cases precipitation may not commence until the neutral point is reached, we have found it difficult to select material for microscopic study which we could be sure was formed under acid conditions. We have selected photographs of two samples which we think have undergone enrichment under acid conditions.

Fig. 2 of Plate I. is a photograph of a polished section of ore collected at the top of the rich ore from the Miami mines, Arizona. Fractured sphalerite is undergoing replacement by chalcocite which in the sample shows no trace of bornite or other minerals. The black in the center is a pit caused by the tearing out of sphalerite. As far as we know, this is the first example of the direct replacement of sphalerite by chalcocite that has been described. Fig. 2 shows fractured bornite cut by veinlets of pure chalcocite from Collahuasi, Chile, which is referred more doubtfully to acid solutions.

Precipitation from neutral solutions may take place throughout a considerable range, provided that hydrogen sulphide and sulphur are only sparingly present in the descending solutions, as the reaction rate is slow between copper sulphate and the metallic sulphides of the hypogene[1] ore. Theoretically at least the chances are better for the development of the intermediate copper iron sulphides in neutral solutions, but on account of difficulties already mentioned, the results of our study do not as yet permit of a definite statement.

In the above, electrolytic solutions are chiefly involved, but as

[1] Ransome's term for ore formed from ascending solutions.

soon as a sulphide precipitate is formed, there is the possibility of further migration in a dispersed condition in acid, neutral and especially alkaline solutions. Since hydrogen sulphide is probably not present in large amounts and under much pressure, and since the chances for liberation are less in the case of descending solutions than ascending solutions, this method is probably not as important as in the formation of hypogene ore.

XVIII. *Enrichment from Ascending Solutions.*[1]

We have every reason to believe that ascending mineral solutions ordinarily carry both hydrogen sulphide and carbon dioxide in abundance, and under pressure, and where minerals like the copper sulphides are involved, so susceptible to transportation and transformation under these conditions, we may expect continued circulation to produce a series of secondary minerals, resulting in the end product chalcocite.

Plate XIV., Fig. D, is presented as an example of the more complicated series, often developing under these conditions. The slide is one of the suite of specimens from the Engels mine, Plumas county, California, described by Professor A. F. Rogers.[1] The chalcopyrite (cp) and the bornite (bo) belong to the first generation of ore minerals and are altering into covellite with a second generation of chalcopyrite (cp_2) and finally into chalcocite (cc). We believe that Professor Rogers presents valid evidence indicating that the later minerals were formed by ascending alkaline solutions.

Mr. J. C. Ray[2] has published the first of his series of studies on the Butte, Mont., ores, which prove that from the start this ore deposition involves a series of enrichments in regard to certain constituents, and a complimentary impoverishment in regard to others. Here the deposition begins with a quartz-pyrite stage which caused an addition of iron and sulphur and a removal of

[1] Turner and Rogers, "A Geologic and Microscopic Study of a Magmatic Sulphide Deposit in Plumas County, Calif., and its Modification by Ascending Secondary Enrichment," ECON. GEOL., 1914.

[2] J. C. Ray, "Paragenesis of the Ore Minerals in the Butte District, Montana," ECON. GEOL., Vol. IX., pp. 463–482, 1914.

the silicate minerals. This is followed by a sphalerite (and galena) stage in which the chief result is the addition of zinc and removal of iron. Enargite then replaced the two former minerals, involving a removal chiefly of iron and zinc and an addition of copper and arsenic. The later changes brought about a subtraction of all other metals except copper, in respect to which the ore is progressively enriched. Sales'[1] structural study and Ray's microscopic work show conclusively that all these changes which are developed in the deep ores are caused by ascending solutions. Many of the complicated structures discovered, suggest to us reactions during a slow crystallization from a colloidal state. Metallographic study[2] is emphasizing that the deposition of the so-called primary (hypogene) ore does not take place at a single stage, but that there are successive replacements of earlier sulphides by the later ores. It is unfortunate that in the best contribution along these lines, Graton and Murdoch[3] have assumed that those copper minerals which are secondary in the mineralogical sense, are also secondary in the geological sense, according to the unfortunate nomenclature now current, that is, deposited from descending solutions.

We conceive that the process of downward enrichment is exceedingly slow,[4] and that the solutions may not be concentrated, and are probably chiefly of an electrolytic nature, while ascending solutions are richly charged with gaseous dispersive agents as well as with metallic sulphides, and that precipitation takes place rapidly with progressive changes in the character of the minerals formed resulting in complicated replacements and reaction structures. If this is true, there should be recognizable differences in the structures of the two types of ores, and Professor Rogers

[1] "Ore Deposits at Butte, Montana," *Bull. Am. Ins. Min. Engs.*, No. 80, pp. 1523–1627, 1913.

[2] For a recent example see Lindgren and Whitehead, "A Deposit of Jamesonite near Zimapan, Mexico," ECON. GEOL., Vol. IX., pp. 443–444, 453–455.

[3] "The Sulphide Ores of Copper," *Trans. Amer. Inst. Min. Engs.*, Vol. XLV., pp. 6–81, 1913.

[4] For geological data see Tolman, "Secondary Sulphide Enrichment." *Min. & Sci. Press*, Vol. 106, pp. 178–181, 1913.

will publish shortly a preliminary statement of certain of these differences. (See Plate I., *d*.) In the laboratories of economic geology at Leland Stanford Jr. University, a series of investigations are nearing completion on those sulphides that, from geological evidence, we believe to be formed from ascending solutions.[1]

F. APPLICATION TO THE FORMATION OF ORES IN GENERAL.

A broad application of the theory of transportation of colloidal sulphides in a dispersed condition is not possible under the earlier ideas that dispersion is prevented by slight elevations of temperature, by the presence of electrolytes in solution, and that colloidal solutions are suspensions of relatively large particles, and therefore cannot penetrate coarse filters or the pores of rocks. Up to date, attention has been directed chiefly to the colloids formed near the surface in the zone of weathering, and the transportation of dispersed sulphides by the deeper ore forming solutions has not been investigated. Krusch[2] suggests the possibility that "gel" ores may be formed by ascending solutions but states that no well established examples of such are known. In the course of the experimental work, temperatures approaching 200° C. were employed, and under these conditions dispersion by hydrogen sulphide is increased. Although we lack a series of experimental determinations of the effect of temperature on dispersion, we can discover no reason for believing the latter will not be active at temperatures at which most ore bodies are formed.

It is even possible that where hydrogen sulphide is retained in solutions under high pressure, dispersion may take place in acid solutions, and under high temperature. It appears probable that we have all gradations in the size of the molecules of colloidal suspension, the smallest of these comparable in size to those of electrolytic solutions. The idea that colloidal suspensions cannot pass through membranes and pores of rocks must be modified, and applies only to dispersions of large molecules, or particles

[1] The term is used in the mineralogical sense.

[2] P. Krusch, *Zeit. f. prakt. Geol.*, pp. 506–513, 1913.

such for instance as colloidal silica at ordinary temperatures and in alkaline solutions. Further, the idea that there is always a well defined gel state which later undergoes crystallization is by no means established. Crystallization may be practically simultaneous with precipitation of the dispersed matter.

There are, however, certain fundamental differences between the two kinds of solutions. Precipitation from an electrolytic solution is often accompanied by, or caused by a chemical reaction. Dispersion, and precipitation of dispersed substances are physical changes, and are often unaccompanied by chemical reaction. Diffusion is active only in electrolytic solutions, and the feeble diffusion that may develop in colloidal suspension, due to enmeshed electrolytes or to other causes, is probably not a factor of importance in ore genesis.

From the above we conceive that colloidal suspension may be more or less heterogeneous, and that the precipitated jelly, or the crystalline precipitate, may also have this property. Precipitation will be most rapid at those points where there is freest escape of volatile dispersing substances, or where the solutions encounter soluble or insoluble precipitating substances. Diffusion of electrolytes into, or out of colloidal precipitates or suspensions, may produce additions to or subtractions from the colloids.

XIX. *Interpretations from Geological Data on the Range of Temperatures within which Sulphide Dispersion is Important.*

Geological data suggest that at the higher temperatures of contact metamorphism and at the high temperatures of the pneumatolytic type of veins, where chlorine, boron and fluorine act as mineralizers and such metals as tin and tungsten are transported as chlorides, fluorides, etc., and deposited as oxides, and at the temperatures at which magmatic segregations of iron oxides are formed, dispersion and precipitation of sulphides is not as important as at lower temperatures. Upon slight lowering in temperature, however, the sulphides appear in abundance, and in the tin veins, the quartz begins to show its character of a coarsely

dispersed colloid, in that much of the quartz is retained within the fissures, and only a relatively small amount of silica is added to the country rock in some cases, while in other cases there is a subtraction of silica.[1]

XX. *Colloidal Characteristics Shown by Veins Formed at Intermediate and Moderate Depths.*

In quartz veins formed at moderate temperatures, such as those included under the "Mother Lode type," the colloidal character of the ore solutions becomes evident. The quartz, the gold, and most of the lead, zinc, and copper sulphides are retained within the fissure, through which the silica cannot migrate. The country rock is pyritized by the escaping hydrogen sulphide, and sericitized by the carbon dioxide and by the potassium salts which diffuse out into the wall rocks; the escape of all these substances bringing about the precipitation of the quartz and sulphides within the fissure.

In veins classified by Lindgren as "metalliferous deposits formed near the surface by ascending thermal waters and in genetic connection with igneous rocks," further characteristics of colloids appear; a persistent gel state being indicated by the fine gained quartz, mixed with chalcedony and opal. Banding throughout the gangue is characteristic but is not of a crustified nature except in vugs. It is caused by alternate zones of chalcedony, chalcedonic like quartz, and occasionally of opal (Fig. 131, p. 563.) Purification of the colloidal gel by crystallization, segregates the impurities in distinctly traceable wavy bands (Fig. 130, p. 563).

[1] For data indicating that in general there is little or no migration of quartz from the fissure into the metasomatically altered country rock, in veins of this type, or the types of veins mentioned below, see: Lindgren, W., "Mineral Deposits," pp. 211–232; *Trans. Amer. Inst. Min. Engs.*, 30, pp. 622, 646, 661, 662, 666–668; Lindgren and Ransome, Professional Paper, U. S. G. S., No. 54, p. 185; Ransome, Professional Paper, U. S. G. S., No. 75, pp. 94–102; Ferguson and Bateman, ECON. GEOL., Vol. VII., pp. 235–251. Even in cases where alteration has raised the silica content of the wall rock, this has been shown, in some cases, to be due to a leaching of the other constituents of the rock, rather than an addition of silica. See Ransome, Professional Paper, U. S. G. S., No. 66, pp. 176–186.

A. N. Winchell[1] found colloidal characteristics so well developed in the rich deposits of the National mine, Nevada, that he describes the ore as an intrusion of a colloidal jelly. In both the types of veins mentioned above, the precipitate is confined to the fissures on account of the abundance of the coarse colloid of silica. In such deposits as these, enrichment can only take place, when subsequent fracturing exposes the enclosed sulphide to attack. Hence the fact that the bonanzas found in ore deposits of the type just discussed are often the result of initial deposition. Large sulphide lodes, without quartz gangue, especially copper deposits, have had a more complicated history, and as the change towards chalcocite is generally accompanied by the development of pore space, these lodes are especially susceptible to both upward and downward enrichment.

As to the method by which ore may metasomatically replace rock, it is only necessary to call attention to Liesegang's[2] suggestive work regarding the reactions between a gel and the adjacent rock, and his full explanation of replacement under these conditions.

XXI. *The Distribution of Ores as Related to the Escape of Volatile Dispersive Agents.*

In deep-seated ore deposits, the hydrogen sulphide must work out against pressure, and therefore a regular deposit of some continuity is to be expected. Where concentrated solutions, highly charged with hydrogen sulphide occur near the surface, a rapid escape of the gas along fissures will occur, and bonanzas of the Comstock and National Nevada types are formed.

As already suggested only a slight change, either physical or chemical, in the character of the country rock may effect dispersion, and account for the remarkable preference of certain ores for one formation over a second, which may show only an insignificant difference from a petrographic or chemical point of view.

[1] Winchell, A. N., "Geology of the National Mining District," *Min. and Sci. Press*, Vol. 105, pp. 655–659 (1912).

[2] "Geologische Diffusionen." The author confines himself to a consideration of the reactions caused by the diffusion of electrolytes through colloids. This phase of the subject was not investigated by us.

XXII. *Limit in Depth of Ore Formation.*

With the exception of "deep-seated" ore deposits such as magmatic segregations, etc., ore formation is a relatively superficial phenomenon, and the depth below the surface at which the formation of ores commence, varies with the type of the deposit. We advance the thesis that the zones of ore formation correspond to the zones of escape of volatile dispersing agents. It is not surprising that the bonanza type of ore deposits found especially in the lavas of the Tertiary period, is limited to a few thousand feet below the surface (seldom over 3,000 feet). The rapid escape of the excessive amounts of hydrogen sulphide from concentrated colloidal suspensions of this type will occur only near the surface. Even in ore deposits formed at greater depths, the gradual escape of hydrogen sulphide is probably a relatively superficial phenomenon.

We believe that experimental determination of the relative dispersion of the various sulphides at a series of temperatures and pressures, will furnish the foundation for a new advance in our knowledge of the science of ore deposits.

SUMMARY.

From the data presented above, we select the following as having most interest to geologists.

I. We are able to form copper sulphides from electrolytic solutions in the following ways: (1) By the substitution of a copper radical for the metallic radical of a sulphide of lower solution tension. (2) Precipitation by amorphous sulphur. (3) By the reaction of a thiosulphate solution upon copper sulphate. (4) Precipitation by hydrogen sulphide. Under favorable conditions, precipitation commences in an acid environment, and reaches a maximum when neutralization is accomplished.

II. In addition to the well-known transportation of copper salts in electrolytic solutions, we were able to dissolve azurite, malachite, and chrysocolla in neutral and alkaline solutions in the presence of carbon dioxide.

III. The proof that, at ordinary temperatures, cupric sulphide decomposes into cuprous sulphide and sulphur has especial geological interest.

IV. We were most successful in transporting copper sulphides, in a dispersed condition, induced especially by the action of hydrogen sulphide, and in precipitating and crystallizing chalcocite by the removal of this gas.

V. We found that certain potassium salts assist in this dispersion, and that certain calcium compounds, and especially aluminum oxide, precipitate them promptly. The penetrating power of the dispersed matter depends upon the size of the particles, and these may approach the size of the molecules of an electrolytic solution.

VI. Upon precipitation, the dispersed sulphides may crystallize promptly, or they may retain the gel condition for a considerable time, during which they may undergo decomposition, or other chemical changes.

VII. From the above, we deduce the theory that the zones of ore formation correspond to the zones of escape of volatile dispersing agents, and the characteristics of ore deposits formed at "Intermediate depths" and "near the surface," are discussed from this point of view.

VIII. *Secondary Enrichment.—Downward enrichment* is initiated in acid electrolytic solutions. With depth and alkaline solutions and dispersion may become factors, but of what relative importance we do not know.

Upward Enrichment.—We believe that many so-called primary ores are the product of successive stages of mineralization, during which they are enriched in respect to certain substances and impoverished in regard to others. At Butte, the series is especially complicated, but the final stages result in a progressive enrichment in respect to copper and impoverishment in respect to all the earlier introduced metals. Alkaline solutions, dispersion, precipitation and subsequent crystallization are of paramount importance here.

DISCUSSION

This department has been established by the editors in order to afford to those interested in questions relating to economic geology an opportunity for informal discussion. Contributions are cordially invited either in the form of discussion of more formal papers appearing in earlier numbers or bearing upon matters not previously treated. Letters should be directed to the Editor, Sheffield Scientific School of Yale University, New Haven, Conn. The full name of the author should be attached to all communications.

THE GENESIS OF THE MACKAY COPPER DEPOSITS, IDAHO.

Sir: In Volume IX, page 347 of this Journal I state that the conception of magmatic emanations as the direct source of lime-silicate rock near igneous contacts "has received much support in recent years particularly in the writings of Lindgren, Kemp, Spurr, Goldschmidt and others, but has been strongly opposed by Leith, Barrell, and recently by Uglow." The last part of this statement should have read "strongly opposed as the dominant process," etc. I am well aware that Barrell (Professional Paper U. S. Geological Survey No. 57) distinguishes clearly between contact metamorphism and contact metasomatism at Marysville, Montana, and that Leith and Harder (Bulletin U. S. Geological Survey No. 338) conclude that the iron ores and some of the associated silicates at Iron Srpings, Utah, represent magmatic emanations. In both papers, however, the development of lime-silicate rock by concentration of impurities in the limestone through reduction in volume is presented as the dominant process. On the other hand in the recent writings of the geologists of the first group most of the lime-silicate rock is credited to direct magmatic emanations. None of them, so far as I am aware, totally disregards, however, the possibility of lime-silicate development by concentration of impurities in the limestone. I do not believe that any observer of either group adheres to one view to the to-

tal exclusion of the other, but they certainly place strong emphasis on different processes. In an effort to bring out concisely the essential contrast in opinion I unintentionally omitted, as courteous letters of protest from Professors Leith and Barrell show, the qualifications necessary to a fair statement of their views.

J. B. UMPLEBY.

THE RELATIONSHIP OF FOSSIL-WOOD TO OIL

Sir: In his memoir on The Oilfields of Burma[1] Mr. E. H. Pascoe offers some remarks on the origin of petroleum, and in discussing the possible nature of vegetable "ur-material" points out that "the extraordinary abundance of fossil wood in the succeeding period seems rather suggestive."

He puts forward the tentative suggestion that "the objection that had petroleum been derived from wood, we should expect to find woody fiber in some quantity in the oil-bearing beds, might be met by the statement that in all probability oil has migrated laterally from synclines or the lower flanks of anticlines up into the crestal portions of the latter, in which case the vegetable fiber would remain widely but sparsely strewn in these synclinal areas."[2]

This assumes the formation of oil in the rocks after their deposition and still leaves unexplained the extraordinary abundance of fossil wood in the *succeeding* period. This association of oil-bearing rocks succeeded by rocks containing abundant fossil wood is not merely noted in Burma but similar occurrences are quoted by Mr. Pascoe both in Assam and in the Coalinga oil district, California (p. 240). It seems to me that the association of oil and fossil wood is not the only significant fact but that the order of succession of oil-bearing beds followed by beds containing fossil wood is highly significant; and viewed from the standpoint that oil may be a sedimentary deposit it to my mind points to a possible explanation that incidentally explains other

[1] Mem. Geol. Surv. Ind., Vol. XL., Part I.
[2] *L. c.*, pp. 239 and 240.

points connected with the oil deposits as well as this succession of oil and fossil wood.

In my paper on "The Sedimentary Deposition of Oil"[1] I pointed out that if oil is of sedimentary origin in deposits and is not a secondary product in them, then it is necessary that the decomposition of the organic bodies should have proceeded elsewhere than in the strata themselves. For this purpose nothing seemed so suitable to me as closed lagoons or swamps.

When vegetable matter decomposes in fresh water swamps or lagoons it becomes carbonized under the action of bacteria. Hoppe-Seyler has shown that under such conditions methane and carbon dioxide also are formed but no higher hydrocarbons.[2]

This action is stopped by brackish or salt water. Züber has shown that under bacterial action in salt water more fatty and tarlike substances are produced.[3]

The possibility that I wish to put forward is that the bacterial decomposition of wood and vegetable matter may have occurred in swamps or lagoons containing silica in solution and possibly also salt.

Under such conditions carbonization to coal and methane and carbon dioxide would not occur but probably more fatty and oily substances would be produced. These bodies would rise to the surface as soon as formed.

The decomposition of the vegetable matter, giving rise also to organic acids, or carbon dioxide or both, would precipitate the silica as a stiff gelatinous substance at the spot where the acid formed.[4] In other words the carbonaceous material of the decaying vegetation might be replaced by silica.

It seems possible therefore that a fatty or oily layer might accumulate on the surface of the swamp while silicified wood still gelatinous or cheese-like in consistency formed at the bottom.

[1] Rec. Geol. Surv. Ind., Vol. XL., Part 4, 1910.

[2] *Zeitschr. f. physiol. Chem.*, 1886, pp. 201, 401.

[3] *Zeitsch. prakt. Geol.*, 1898, p. 84.

[4] See: Julien, *Proc. Amer. Assoc.*, XXVIII. (1879), p. 396; Sollas, *Ann. Mag. Nat. Hist.*, Nov., Dec., 1880; J. Rothe, *Allgem. Chem. Geologie*, p. 576; Le Conte, *Amer. Journ. Sci.*, 1880, p. 181; A. Geikie, "Text-book of Geology," p. 612.

On such a swamp or lagoon being drained off and denuded, first of all the fatty or oily layer would drain off and become incorporated in the neighboring sediments and then at a later period the silicified wood would be removed and incorporated in the sediments, giving a series of sediments containing oil followed by sediments containing fossil wood.

From the consideration of the facts in Burma it does not seem impossible that some such thing occurred.

The Arrakan Yomahs were first uplifted in Eocene times if not before. The rocks composing them are much indurated and infiltrated with silica pointing to the possibility of siliceous springs having existed over the area. Salt springs are also abundant.

The gradual uplift of the range during the Himalayan uplift would drain off any siliceous lagoons or swamps such as might be expected to have formed and would, if my suggestion is correct, account for the appearance of first of all oil in the deposits and at a later period of silicified wood.

If any fresh water swamps or lagoons also occurred, then ordinary carbonization would also occur and we should expect to find some coal seams in the neighboring deposits, which is actually the case.

The occasional association of oil and coal is therefore to be expected; neither is the parent of the other but they would be cognate in this case. In support of this suggestion I would quote Theobald.[1] He was of opinion that the fossil wood in Burma was formed in the following way:

> The trunks of trees in question floated about till water logged in shallow lakes, in which, on sinking, they became mineralized through the agency of springs holding silica in solution.

Possible chemical change in the oil after its deposition in the sediments is to my mind not only possible but highly probable under the differences in temperature and pressure conditions it must necessarily have undergone.

The only difficulty is the present form of the silicified wood.

It is found as trunks of trees or portions of trunks with mere

[1] Mem. Geol. Surv. Ind., Vol. X., p. 64.

stumps of branches, having in fact "the appearance of drift wood which has been denuded of most of its branches by decomposition and rough treatment in swirling waters, sinking when waterlogged and being rapidly covered by sand banks."[1]

It is impossible to conceive hard silicified wood being transported by water without showing much more wear and tear and some of the longer trunks could not possibly be rolled by water without being broken in the process; but it is just conceivable to me that at the time of denudation of the lagoon sites the siliceous wood was still gelatinous or cheese-like in consistency and so might more easily be transported with only the loss of branches, etc., the final hardening into stone taking place after its deposition in the sediments; just as the gelatinous silica precipitated from solution by certain algæ first slowly loses part of its water and becomes cheese-like and then at a later period hardens into stone.[2] The gelatinous form with its included water being of lower specific gravity than the final hardened stone, the transportation of the still gelatinous silicified tree trunks would be comparatively a simple matter.

The above theory is merely tentative but it seems to be a possible simple explanation of the presence of oil-bearing deposits without traces of woody fiber in the same deposits, followed by fossil-wood sands without oil. It also explains the occasional association of oil and coal deposits, and it is supported by the sequence of events known to have taken place in the upheaval of the Arrakan Yomahs.

In my paper on "The Sedimentary Deposition of Oil" I excluded limestone oils and for the same reason I do not consider that the Eocene limestone oils come into this question.

MURRAY STUART.

[1] Pascoe, *l. c.*, p. 41.

[2] W. H. Weed, Ninth Ann. Rep. U. S. G. S., 1889, *Amer. Journ. Sci.*, XXXVIII. (1889), p. 351.

REVIEWS

Lindley on Mines. A treatise on the American Law Relating to Mines and Mineral Lands Within the Public Land States and Territories, etc. By CURTIS H. LINDLEY. Cloth, octavo, three volumes. San Francisco, Brancroft-Whitney Company, 1914.

This is the third edition of the most comprehensive treatise on American mining law. The first appeared in two volumes in 1897, when the subject was in its formative stage and when miners and courts alike were still uncertain as to many of the principles ultimately to be established by the supreme court. The second, much enlarged, was published in 1903, and has remained the standard text-book on the subject, although the plates and stock in hand were destroyed in the San Francisco fire in 1906, and the work has therefore been out of print and practically unobtainable for the past several years.

The relation between geology and law is not always apparent on casual consideration; yet the laws of mankind govern every phase and manifestation of human activity. The lawyer must at some time or other come in touch with every branch of art, science and industry, and master for himself the sum of human knowledge. Thus it should never surprise a jurist to be confronted with learned propositions in any field of modern investigation. He may be led into the realm of medicine, wherein are required an understanding of anatomy, surgery, physiology and toxicology; or into the domain of chemistry where he will need to study metallurgical processes and the elemental constitution of matter; or into the field of mining and a consideration of questions of mineralogy, geology, and the structural relations of ore deposits. But, on the other hand, the geologist may be greatly surprised to be told that his chosen science is so broad as to require, in at least one direction, and in one of its most practical applications, a certain amount of familiarity with the statutes and judicial decisions of different countries. A law course is not ordinarily included in the curriculum leading to a Master's degree in geology. Indeed, geologists are commonly but little acquainted with legal principles of any description. There is, however, a peculiarly intimate relation between mining law as enacted and interpreted in the United States and the work of the economic geologist who is called upon to untangle the complex relations of veins and other ore bodies located under the federal mining statutes. The services of our most celebrated geolo-

gists are often called for, and some of the most learned and interesting dissertations have been given in the court room, instead of in the class room or in print.

The importance of the service rendered by the geologist to the miner is recognized not only by mining companies, as shown by the increasing tendency toward the establishment of regular geological departments in connection with the larger mines, but also by the lawyers who are familiar with the practice of mining law. On this point Judge Lindley speaks as follows (p. 147):

"A practical knowledge of what we may term structural geology, derived from actual contact involved in the investigation and working of mines, is quite as essential as a familiarity with the law, in order to enable one to present any satisfactory illustration of the nature of the things to which the law is to be applied. Lawyers specializing on the legal phases of mining law necessarily absorb some general information from the mining engineers with whom they are brought in contact. But as a rule this familiarity with structural conditions is to a large degree superficial. The mining engineer and expert with a broad experience, not only in the field of mining operations, but in mining litigation, occupies a unique position, not only as the mentor of counsel, but as an important aid to the court in the ascertainment of the facts to which the law is to be applied."

And in speaking of the United States Geological Survey, we find the following well-merited tribute (p. 177):

"The conscientious work of this magnificent organization is a monument to the industry, scientific attainment and continued devotion to the public service of the groups of men who organized and carried on the great work. The benefit accuring to the mining industry has been incalculable."

No adequate analysis of the elaborate discussions upon all branches of the subject contained in this work can be presented within the limits of an ordinary review. It is intended for a book of reference, and its object is kept in mind throughout. Thus, the table of contents with which it opens occupies 44 pages; a table of cases cited in the text, alphabetically arranged, requires 196 pages; a brief presentation of the mining laws of other lands which may have had some influence in the adoption of the principles underlying our own laws occupies 32 pages; a historical review of the federal and state legislation concerning mineral lands is given in 72 pages; 412 pages are devoted to consideration of the lands subject to appropriation under the mining laws and the persons who may acquire rights therein; state and local district regulations are discussed in 92 pages; it requires 560 pages for a presentation of the subject of the acquisition of title to public mineral lands by location; 450 pages to analyze the title acquired and the rights conferred by location; 287 pages

to relate the law as to the proceedings for obtaining United States patent and discuss the title conveyed by that instrument; nearly 700 pages for discussion of incidental questions and the text of the mining statutes themselves; and 192 pages for the very satisfactory and complete index. The treatise is admirably constructed and arranged to save the time of the consulting student, with black-faced chapter and paragraph titles, subject references at the top of each page and copious citations in foot-notes of all authorities cited in the text. Typographical erors, although noticed occasionally, are few.

The literary style of the author is conspicuous for its elegance of diction, and his arguments are lucid and unambiguous, even to a reader unaccustomed to legal verbiage. The latest opinions of the state and federal courts are presented and analyzed, and their trend clearly shown; and the rulings and regulations of the land department are likewise given full attention. When considering decisions which do not square with the principles of the mining laws already established in whole or in part Judge Lindley does not hesitate to differ respectfully but firmly with the learned judges and courts from which such challenged theories and decisions have emanated. He points to cases in which both courts and writers of text-books have rendered conflicting opinions and indicates the principles likely to prevail in the end. Thus, although the author himself, in his first edition, expressed the belief that "under no circumstances could there be any extralateral right attaching to a location where the vein on its course enters and departs through the same side line," and although he criticises the decision of the trial court in the Providence-Champion case, yet he now gives it as his opinion (p. 1378, footnote) that "the modern tendency of decision is to apply to all secondary veins at the points of departure planes parallel to the end lines controlling extralateral rights on the original vein."

It is well known to students of the subject that the farmers of the mining law had in mind ideal conditions, in which each vein should pursue a perfectly straight course upon the surface of the ground, in strike and dip should be parallel with every neighboring vein and should be so located that it passed through both end lines of the claim. "It is upon the existence of such a theoretical lode and hypothetical location that the existing laws were framed. As Dr. Raymond facetiously remarked:

"'If all mining properties presented this beautiful simplicity of structure, and all mining locators exhibited a corresponding simplicity of purpose, the application of the law would be easy. But the *naïveté* of the statute fares badly between the freaks of nature and the tricks of man.'" (Lindley, p. 1331.)

Instead of ideal simplicity we find every conceivable complication. Whether a given lode location has or has not extralateral rights depends

upon the relation of the apex of its discovery vein to its surface boundaries, and the parallelism of its end lines; and the extent of its extralateral rights depends upon its length of apex on the discovery vein. But, if it does possess extralateral rights, it has them also for all other veins which apex within its bounding lines, the rights on each vein depending on its length of apex. Now, when it is considered that each and all of these veins may intersect each other upon strike and dip, and may cross or unite with all the veins of contiguous claims at various depths beneath the surface, and that the lines of two or more claims may be so laid upon the apices of any or all of these veins as to include the same ore bodies within the planes of their end lines extended in their own directions; that faults of equally diverse strike and dip and varying amount of displacement are numerous in nearly every important mining camp; and that the surface lines of conflicting and overlapping lode locations cross each other in all directions like a pile of jack straws, it begins to be evident why so much of the time of the courts in western mining states is taken up by mining litigation. And the value of such a treatise as the one under review becomes at once apparent.

Diagrams presented, illustrating the conditions of the more important cases and the contentions of the respective litigants, serve to show also the rules adopted by the courts in all of the situations which have thus far arisen and been adjudicated. Careful study of these cases as reported and discussed by Judge Lindley should enable any mine owner or engineer to determine for himself whether the complications existing in his mine have arisen heretofore, and if so what are his rights in the premises. The rules given by Lindley are those which are clearly indicated by the decisions of the courts, and reference is always given to the volume and page where the full text of the opinion may be found. It is needless to say that his work has long been looked upon as an authority and has been quoted by learned judges in rendering their verdicts. Thus his opinion has weight in connection with propositions wherein there is as yet no final ruling by the supreme court. Such an instance is in connection with the requirement of the statute that the end lines of a claim must be parallel in order that it may have any right of extralateral pursuit. Judge Lindley remarks (p. 1300):

Where, however, the two lines crossing the lode converge in the direction of the dip, intersecting, as they are produced, at some point beyond the side-lines, we cannot see upon what principle the doctrine can be maintained. Where the reason of the rule ceases, the rule itself should cease. To say to a claimant with converging end-lines, "The law permits you to take as much of the vein in its downward course, beyond the side-lines, as you may include within the parallel end-lines. You have taken less than you might have acquired; therefore you shall have nothing," is illogical.

And, although the California courts have in some instances inclined to the opinion that a claim with converging end lines has no extralateral rights, yet Judge Lindley says that "The question, therefore, as to whether any extralateral right is to be awarded in cases of converging end-lines on locations made under the act of 1872 is *res integra,* so far as the courts are concerned"; and gives it as his firm opinion that in such cases extralateral rights do obtain.

His statement as to the rule that end lines "must be straight lines, not broken or curved" does not seem to be made with quite the usual full consideration of all possible conditions. It is true that he says in another place (p. 1296): "When we speak of end-lines we mean such lines as are crossed by the lode on its course"; and it may be thus inferred that a claim with broken end-lines but with portions of the two end-lines parallel and those parallel portions crossed by the apex of the vein, would still have extralateral rights. But his language as it stands would seem to negative that proposition. No special discussion is presented of the situation arising where the apex of a primary vein crosses one end line and one side line of a claim patented with end lines which diverge in the direction of the dip.

To the lawyer, the mining engineer or economic geologist, to the mine owner or superintendent who desires to have in his possession an authoritative book of reference to which he can go for up-to-date information as to any vexed point in the mining laws of our country Lindley on Mines is indispensable. The thanks and appreciation of all these classes of men are due the author for the painstaking labor and intelligent interest with which the masterly work has been prepared, and to the publishers for care and good taste in its production.

HORACE V. WINCHELL.

SCIENTIFIC NOTES AND NEWS

MR. J. B. TYRRELL has been making an examination of the Puget Formation in southern British Columbia for the purpose of determining the origin of the seepages of oil which occur in it. and the possibility of the occurrence of oil in commercial quantities.

MR. WALLACE E. PRATT has been made Chief, division of mines, Bureau of Science, Manila, effective June 16, 1914, following the resignation of Dr. Warren D. Smith, who has accepted the Chair of Geology, University of Oregon, Eugene, Oregon.

MR. VICTOR C. LEDNICKY has been appointed to a position on the staff of the division of mines, Bureau of Science, Manila, and will leave his present work in Honduras immediately for the Philippines.

MR. FRANK T. EDDINGFIELD, who recently resigned his position in the division of mines, Bureau of Science, Manila, has arrived at his home in Washington, D. C., after a short vacation in Europe.

THROUGH THE GENEROSITY of Sir Robert Hadfield, honorary member, the directors of the American Institute of Mining Engineers are enabled to announce the Hadfield Research Prize of $1,000 for the best contribution to the publications of the Institute upon the general subject of The Different Forms and Combinations of Carbon with Iron, including those in Iron Alloys. The prize will be awarded at the annual meeting of the institute in February, 1916, to the best paper upon this subject which is

[1] Geologists, mining engineers and others interested in applied geology are invited to keep the editor informed of new investigations of mining districts or scientific studies undertaken by them, together with such other scientific and personal items as may come to their notice.

presented to the institute before November 1, 1915, provided such paper is deemed worthy by the Institute's Iron and Steel Committee.

C. T. GRISWOLD is now at the Pittsburgh office of The Associated Geological Engineers, having returned from examining several gold prospects in the Sudbury Mining District.

THE SIXTH INTERNATIONAL CONGRESS of Mining, Metallurgy, Engineering and Economic Geology was held in London between July 12 and July 17, 1915.

A MEETING of the American Institute of Mining Engineers was held in Salt Lake City, Utah, August 10–14, 1914. The meeting was largely attended and many papers of interest were presented. In addition to the technical sessions, excursions were arranged to the mines of Bingham and Park City, Utah, the plant of the American Smelting and Refining Co. at Murray, Saltair, Cottonwood Cañon and other localities. A banquet was held on Friday, August 14, at the Hall Utah.